

Fifth Edition

THERMODYNAMICS

Principles Characterizing
Physical and Chemical Processes

Jurgen M. Honig



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Jurgen M. Honig

*Department of Chemistry,
Purdue University,
West Lafayette, IN,
United States*



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General Commentary

Thermodynamics is generally regarded as a rather arcane discipline: beginners in this area, in particular, find the entire structure rather austere, and have trouble “wrapping their minds around the subject matter”. All too often they tend to think that - somehow - by finding the right formulas and using correct calculational procedures, thermodynamics provides answers that are going to be useful. In what follows I will try to emphasize that by consistent application of a few fundamental concepts the mystery that seems to surround the subject can be unraveled. The fundamental principles and ideas will be introduced as soon as the relevant background information has been supplied. Be on the lookout!

Preface

The fifth edition of my *Thermodynamics Monograph* has been generated at the suggestion of Elsevier Publishers. The major changes occur in Chapter 1, Fundamentals, Chapter 7, Critical Phenomena, and Chapter 8, Topics Related to Critical Phenomena. These now include a fairly detailed description of how some very fundamental physical measurements can be linked to thermodynamic concepts such as temperature, energy, and entropy. The description of the Ising model has been considerably enlarged to deal with certain fundamental and descriptive aspects of critical phenomena and with homogeneity requirements. Materials originally constituting Chapter 8, Topics Related to Critical Phenomena have been replaced by an approach to chaos theory and by a review of Fisher Information Theory, the latter to provide a thermodynamic approach that unifies fundamental tenets of physical phenomena.

As in the earlier versions of the monograph, I adopted a stepwise, incremental approach to every topic under discussion, consistently trying to avoid the use of the “it can be shown” mantra. To ease it into the laws of thermodynamics, I started to be a bit chatty at the outset. As in the earlier editions, I attempted to do better than to simply generate a linear superposition of preceding books and monographs on thermodynamics. Among the other features, I have carried over from the fourth edition methodologies not generally encountered elsewhere. These include the treatment of irreversible phenomena at an early stage, effects of centrifugal fields, a discussion of anisotropic phenomena, a treatment of electron interactions in solids, order–disorder theory and applications, electronic phase transitions, reentrant metallic characteristics, and a primer on critical phenomena.

Mistakes in the presentation of the great expanse of thermodynamics are inevitable; the best I can do is to request that you, as a reader, draw my attention via jmh@purdue.edu, or 765-497-4455, to places where I have been remiss, in hopes that I can provide corrections at an early stage.

I again acknowledge my indebtedness for the friendly guidance and extensive discussions with present and former colleagues the late Profs. A.W. Overhauser, Ben Amotz, J.W. Richardson of Purdue University, and Prof. Józef Spalek at the Jagiellonian University in Kraków, Poland.

It remains to thank the staff of Elsevier, Inc. Anneka Hess, Susan Ikeda, Kumar Anbazhagan, and Swapna Praveen who have been most helpful in getting the present version to press. In addition, as always, I remain resolutely grateful to my extended family, especially to my lovely wife Jo, for bearing with me when I seemed excessively immersed in concepts far removed from her interests in writing, music, and painting.

Jurgen M. Honig
July 2020

1.1 Introductory Definitions

We begin with a boring set of commentaries—a set of definitions, so that we all know what we are talking about. If you do not want to wade through a welter of what seems like superfluous information, you can skip this section, but at least be aware of the distinction between quasi-static and reversible processes. Also, you should be motivated to ponder the statements at the conclusion of this section.

The definitions of relevance are listed below:

System: A material object that exists in space as a useful subject of scientific study; it is set apart for that purpose from the remainder of the universe.

Surroundings: Regions outside the system which, by reason of interactions, bring about changes in the system.

Comment: The system and attached surroundings form an *isolated unit* that exists apart from anything else in our universe.

Boundaries: Regions separating a system from its surroundings.

Comment: It is very important to set boundaries properly and to distinguish appropriately between system and surroundings. This may not always be easy. In many cases, one encounters a gradation of properties as one approaches the boundary, which requires special handling, as in Chapter 5. Often the problem is disposed of by taking the system to be so large that boundary effects may be ignored. Boundaries may be real, such as walls, partitions, edges, and the like, or may be conceptual, such as geometric surfaces.

Body: The content of a specific system.

Comment: To be amenable to thermodynamic investigations, an actual body must comprise sufficient material, such that fluctuations in properties do not dominate and that physical measurements performed on the body do not significantly perturb its properties. The volume of such a body must generally be at least of the order of $10^{-15}/\text{cm}^3$.

Homogeneous vs heterogeneous systems: Homogeneous systems are uniform in properties over their entire physical extension. Otherwise such systems are heterogeneous.

Subsystem: A portion of the region of a system singled out for special study.

Isolated systems: Systems totally unresponsive to any changes that take place in its surroundings.¹

Open (closed) systems: Systems that (do not) participate in the transfer of matter to or from the surroundings.

Comment: A closed system may nevertheless be subject to alteration in its properties by external agents such as electric or magnetic fields, or through irradiation without any transfer of matter across its boundaries.

Permeable (semipermeable) boundaries: Boundaries that enclose an open system (that permit passage of certain chemical species while excluding other species).

Adiabatic systems or processes: Systems whose properties remain unaffected during heating or cooling of the surroundings.

Comment: A scientific definition for an adiabatic system or process is provided in Section 1.7.

Phase: A physically and chemically homogeneous macroscopic region of space within a system.

Comment: In a system, there may exist several subregions in distinct states of aggregation or composition or properties, forming different phases.

Diathermic boundaries: Boundaries that prevent exchange of matter between systems and their surroundings but that permit systems to respond to heating or cooling of the surroundings.

Thermodynamic properties: Physical or chemical attributes that specify the characteristic macroscopic properties of a system.

Thermodynamic equilibrium: A state of a system where, as a necessary condition, none of its properties changes with time.

Comment: It is generally not a simple matter to determine whether a system is at equilibrium. One method, described later, involves subjecting the system to some process that takes it away from its quiescent state under a set of prescribed conditions. If, on release of the constraint, the response is out of proportion to such a process, or if the system does not then return to its original state, it could not have been at equilibrium. If the system does return to its initial state without incurring any other changes in the universe, then it is said to be in equilibrium with respect to the tests that have been conducted. It may be very difficult to decide whether equilibrium prevails in systems subject to very sluggish processes. In such situations, one attempts to establish or calculate a relaxation time over which significant changes in properties are detectable when the system is externally perturbed. It is generally agreed that equilibrium prevails when no changes can be detected after different alterations of the properties are attempted over intervals extremely large compared to the relaxation time.²

Reservoir and surroundings: An external source or sink employed, through appropriate interactions, to alter the properties of a system. A reservoir is assumed to be of such immense size and complete uniformity that its intensive properties (see below) remain uniform, and normally, unaltered in all interactions with the system.

Comment: In studying properties of a system, it is tempting to assign a minor role to surrounding reservoirs, but as we shall see, in many cases their role is just as important as those of the system. We shall later also introduce the assumption that all processes in the reservoir occur reversibly (more on that below).

Thermodynamic coordinates, thermodynamic variables, and thermodynamic degrees of freedom: All three designate linearly independent experimental macroscopic variables that are employed to characterize the state of a system.

Comment: A minimum number of such variables are required to specify systems at equilibrium; their values do not depend on the manner whereby the equilibrium state is reached.

Intensive (extensive) variables: Variables whose values are independent of (depend on) the size and/or quantity of matter contained in a system under study.

Macroscopic (internal) variables: Quantities on a macroscopic scale, which may be directly (only indirectly) placed under experimental control through manipulation of the surroundings.

Comment: Examples in the former category are the volume, surface area, magnetization, or electric polarization of the object under study. These quantities are measured by adjustment of physical size,

state of subdivision, imposition of a magnetic field, or imposition of an electric field. The latter category encompasses changes in properties such as resulting from the heating of an object maintained at a constant volume. All these changes in properties proceed as a result of interventions by the experimentalist. More discussion on this topic is provided in Section 1.7.

State space, configuration space, and phase space: An abstract space spanned by coordinate axes, one for each thermodynamic coordinate, on which a given point represents the numerical value of that coordinate. A hyperspace is then formed by a mutually orthogonal disposition of these axes about a common origin.

Representative point: A point in phase space that corresponds to the state or characteristics of the system for which the state space was constructed.

Path: A succession of states in phase space, or more generally, in physical characteristics, that corresponds to the change in properties as a system passes from a given initial to a given final state.

Quasi-static process: One that involves a slow passage through a large succession of very closely spaced equilibrium states. In this process, the surroundings and/or system are altered such that on the return path to the original external configuration, the universe ends up in a different state.

Reversible process: One whose path may be exactly reversed though a succession of very closely spaced equilibrium states; on conclusion of this process, both the system and its surroundings are restored to their original state.

Comment: The distinction between quasi-static and reversible processes may be illustrated by considering the magnetization of a paramagnetic as compared to a ferromagnetic material. In a paramagnet, the gradual application of a magnetic field slowly magnetizes the sample, which can then be completely demagnetized by slowly eliminating the magnetic field—this process is reversible. A ferromagnet can be slowly magnetized by gradual application of a magnetic field, but on gradual elimination of the field, the material remains partially magnetized. Here, a succession of equilibrium states, followed by the reverse, leaves the system in an altered configuration. This is an example of a quasi-static process. Reversible processes are necessarily quasi-static, but the reverse may not hold.

Steady-state processes: Processes which do not alter the state of a system but do change the surroundings.

Comment: Under steady-state conditions, inputs and outputs of the system remain in balance so that the properties of the system are not altered, but changes do occur in the surroundings as a result of such processes.³ A scientific characterization is provided in Section 6.4.

Number of independent components: The least number of chemically distinct species whose mole numbers must be specified to prepare a particular phase.

Comment: Due account must be taken of any prevailing chemical equilibria; for then, the concentrations of the various participating species cannot all be independently altered. This matter will be fully discussed in due time.

Number of degrees of freedom: The number of state variables that can be altered independently and arbitrarily, within limits, without changing the number of phases within the system.

Generalized force and pressure: This is the application of an agency whereby the state of a system is altered by external intervention.

Comment: As the most elementary example, used in the next section, one may cite the placement of a weight on top of a body in the earth's gravitational field. The force is then specified by mg , where m is the mass of the weight and g is the gravitational constant. An early example is the mechanical pressure exerted on the system of interest, defined as the force per unit cross-sectional area exposed to the force. More general examples of forces are provided in Sections 1.4–1.6.

Functions of state: This concept refers to a very important distinction between two types of mathematical entities used to describe changes in the state of a system: quantities whose changes depend on the specific path involved in forcing the change, and quantities that depend solely on their initial and final configurations of the system involved in the change. The latter mathematical objects are known as *functions of state*. Clearly, it is of immense value to deal solely with the second category because it obviates the need to consider how the change is accomplished. In our early development in thermodynamics, we will deal with procedures for generating functions of state from empirical observations. We will repeatedly pound this point home. A better definition for functions of state is to be found in Sections 1.5–1.6.

Before proceeding, it is assumed that the concepts of mass⁴ and volume are elemental. The mass corresponds to the amount of matter in the body under study (leaving aside complications that arise when relativistic effects need to be taken into account). The volume V cited in the next section is that which corresponds to the physical extension of the body under study. Much of the initial discussion will be based on these two concepts.

As already implied, but reiterated here for emphasis, is the fact that the processes taking place in the surroundings usually cannot be ignored. These events are often just as important as those in the system proper. This will become evident in the study of Sections 1.9–1.10.

Remarks and Queries

- 1.1.1. The universe is an excellent paradigm of an isolated and a closed system. Ordinarily, events occurring at astronomical time scales may be ignored in dealing with physical and chemical processes occurring in the laboratory.
- 1.1.2. As an example of problems involving long time scales, consider the reaction of hydrogen and oxygen in a balloon at room temperature. The fact that there seems to be no detectable change in the concentration of either constituent over many months does not mean that the system is equilibrated: insertion of platinum black as a catalyst leads to a measurable rate of formation of water, and heating the balloon with a torch leads to a disaster.
- 1.1.3. As an example, consider the passage of current from a battery through a conductor. At a steady state, the average electron density in any section of the material remains invariant; also, the initial rise in temperature due to Joule heating stops when the rate of heat generation is exactly compensated for by the radiation of heat into the atmosphere. Thus, under steady-state conditions, the material properties of the conductor during this process do not change with time, but the surroundings are altered: the battery runs down and the air is heated up.
- 1.1.4. This is not necessarily always the case: there are instances where mass cannot be directly correlated with the “amount” of matter. For instance, nuclear transitions may occur between energy levels so different that the change in mass due to relativistic effects ($E = mc^2$) has to be taken into account. Fundamentally, only energy is the truly relevant conserved quantity. We do not explore the ramifications of relativistic effects here.
- 1.1.5. Is it appropriate to classify a definition as being correct or incorrect? Conventional or unconventional? Complete or incomplete? Consistent or inconsistent?
- 1.1.6. Cite conditions under which a proffered definition may be rejected.

1.2 The Zeroth Law of Thermodynamics

We start here with a consideration of general thermodynamic laws that govern all possible processes in the universe. These laws are the fundamental building blocks on which all of thermodynamics rests; they deserve our full attention. Do not be discouraged by a certain degree of abstraction; things will get better later.

The first of these principles invokes transitive properties (see below) that characterize the interactive processes carried out in succession. Its main power derives from the fact that we thereby can set up the so-called equations of state for any material and generate a thermodynamic temperature scale.

We begin by positing the so-called *zeroth law of thermodynamics* in a familiar and sensible formulation which asserts that

Two bodies in equilibrium with a third are in equilibrium with each other.

To study the implications of this seemingly obvious statement,¹ consider the special case where the mechanical properties of a system can be characterized solely in terms of a prevailing pressure P and volume V . While V is well defined, the concept of pressure, briefly introduced in the last section, is related to the description of forces in Section 1.4; here, it is the force per unit area at which the system is maintained at volume V .

We follow the procedure advocated by Buchdahl.² Consider two systems 1 and 2 that are initially isolated; let P_1 and P_2 be the pressures whereby the systems remain at fixed volumes V_1 and V_2 . Proper adjustments must be made to permit physically possible pairs of pressure–volume variables (P_1, V_1) and (P_2, V_2) to be independently established. Let these two units so constructed now be joined to form a compound system and equilibrated. It is an experience of mankind that only three of the four variables can then be independently altered. We take account of this restriction by setting up a mathematical relation $\beta_3(P_1, V_1, P_2, V_2) = 0$, where β_3 is just a fancy label for the particular mathematical function needed to specify the interrelation between the indicated variables; its detailed form is not of interest at this point.

We now repeat the process by joining system 1 to a new system 3 characterized by the pressure–volume variables P_3, V_3 . By the same line of argument, after equilibrating the compound system, we encounter another interrelation of the form $\beta_2(P_1, V_1, P_3, V_3) = 0$. Lastly, on joining systems 2 and 3, we must set up a third mathematical restriction of the form $\beta_1(P_2, V_2, P_3, V_3) = 0$. If equilibrium prevails after establishing each combination, we require for consistency with the zeroth law that system 3 remain unaltered in its union with either system 1 or 2. This has an interesting consequence: for, we are allowed to solve the equation $\beta_1(P_2, V_2, P_3, V_3) = 0$ for P_3 in terms of P_2, V_2, V_3 , as well as the equation $\beta_2(P_1, V_1, P_3, V_3) = 0$ for P_3 in terms of P_1, V_1, V_3 . These solutions take the form $P_3 = \Phi_1(P_2, V_2, V_3) = \Phi_2(P_1, V_1, V_3)$. From this relation, we now construct the following difference function, which we call λ , to wit:

$$\Phi_1(P_2, V_2, V_3) - \Phi_2(P_1, V_1, V_3) \equiv \lambda(P_1, V_1, P_2, V_2, V_3) = 0. \quad (1.2.1)$$

The prescribed construction of the function λ unfortunately generates a glaring inconsistency: the functional dependence of λ on V_3 is absent from the function $\beta_3 = 0$; also, it makes no sense to have to refer to system 3 when combining systems 1 and 2. To resolve this difficulty, we introduce a new requirement: we demand that V_3 is present in the functions Φ_1 and Φ_2 in such a manner that V_3 is eliminated when the difference between Φ_1 and Φ_2 is constructed. This is achieved in most general terms by requiring that the functions Φ assume the forms $\Phi_1 = f_2(P_2, V_2)h(V_3) + q(V_3)$ and $\Phi_2 = f_1(P_1, V_1)h(V_3) + q(V_3)$, where h and q are the *arbitrary* functions (any functions you please) of V_3 , that serve

to separate out the V_3 dependence. Substitution of the last two equations in Eq. (1.2.1) then leads to the relation

$$f_1(P_1, V_1) = f_2(P_2, V_2). \quad (1.2.2a)$$

Similarly, consistent with the zeroth law, we find that

$$f_1(P_1, V_1) = f_3(P_3, V_3). \quad (1.2.2b)$$

These results are sensible: reference is now made only to variables appropriate to each distinct combination. Equations (1.2.2a) and (1.2.2b) thus characterize the equilibration condition. Moreover, this process permits us to select system 1 as a reference standard to infer whether systems 2 and 3 are in mutual equilibrium, accordingly as system 1 is or is not changed when placed in contact with first with system 2 and then with system 3.

Empirical Temperatures and Equations of State

Clearly, in the above discussion, the functional interrelation $f_1(P_1, V_1)$ has been assigned a special role, in serving as a reference standard. It therefore makes sense to provide for this function a special symbol, τ_1 , that serves as a short-hand notation: more generally, we write $\tau_i = f_i(P_i, V_i)$, where τ_i is called the *empirical temperature (function) for system i*.

The introduction of τ involves a certain degree of malice of forethought: it is supposed to evoke the concept of hotness levels. If we choose a gas as a working substance and rigidly fix its volume, then its pressure varies with hotness levels and can thus function as a measure of hotness. Alternatively, we can fix the pressure and monitor the change of volume with an adjustment of hotness. The processes involved in generating a quantitative scheme linking τ to changes in P or V will be explored after setting up the first and second laws of thermodynamics. Here we note only that the ideal gas is a useful abstraction approximated by inert gases at high levels of hotness and low pressures—*He* in particular, because of its inertness over a wide range of P or V alterations, and because of the simplicity of the expression linking τ to P and V , and the relative ease with which such changes can be measured. The explicit display of

$$\tau = f(P, V) \quad (1.2.2c)$$

is known as an equation of state and τ , as an empirical temperature.

Before proceeding we should note that there is nothing sacred about the use of pressure and volume of ideal gases in generating a viable temperature scale. A plethora of empirical methods are in use for measuring hotness levels. These involve comparing and extending any proposed measuring methodology with the temperature scale setup below for the ideal gas. This calibrated scale can then serve as a reference and source of extension for another methodology, and the process can be repeated as desired to cover a very large range of hotness levels. Incidentally, many of the techniques involve monitoring changes in physical properties that are not linear, in contrast to the method detailed later. One thereby generates a set of empirical temperature scales, with the associated problem of unifying these diverse scales so as to attain a unique description—a matter that is resolved next.

The labeling of τ as a “temperature” is obviously meant to link the physical properties of a system to human sensory perception of “hotness levels.” Minimally one should ask that the designated temperature should increase monotonically with increasing hotness levels. This quantification scheme involves use of an appropriate equation of state of the material as an indicator of hotness. An enormous

multitude of indicators have been used for this purpose, such as the volumetry of inert gases, resistivity of solids, viscosity of liquids, spectral emissivity of solids, thermoelectric voltages, sound velocity, and magnetic susceptibility. The methods of measurements and the experimental precautions required to attain reproducible results are listed in special compendia.³ It is thus sensible to pick from the set of temperature detection methods a reference standard that is inert, of particular simplicity, that can be universally extended over a large range of hotness levels, and that can be easily linked to fundamental concepts such as the laws of thermodynamics. As stated previously, the system appropriately suited for this purpose is the ideal gas, the properties of which are well approximated by *He* gas at elevated hotness levels and low pressures, where small deviations from ideal behavior can be corrected for.

So, how do we proceed to construct a viable equation for ideal gases linking τ to P and V ?

It has been known for over three centuries (Boyle's law) that the product PV is constant at fixed hotness levels well above those required to liquefy the gas. This allows us to adopt the PV product as the appropriate measure of choice for empirical temperatures.

An Absolute Temperature Scale

In many temperature determinations, one maintains the gas thermometer at a fixed low pressure. A useful quantification scheme is the so-called *Celsius* scale that assigns the values $\tau = 0^\circ\text{C}$ (this was the original intent, but nowadays the standard value is $\tau = 0.01^\circ\text{C}$) and $\tau = 100^\circ\text{C}$ to the *He* gas thermometer maintained at equilibrium respectively with water containing ice and with water equilibrated with steam maintained at 1 bar.⁴ Let the volume of helium gas in a flexible container at a fixed low pressure be the indicator of hotness levels, such that the measured volumes V , V_0 , and V_{100} correspond to temperatures τ , 0, and 100°C respectively; then τ is to be specified by

$$\tau = 100 \frac{V - V_0}{V_{100} - V_0} = 100 \frac{V}{V_{100} - V_0} - 100 \frac{V_0}{V_{100} - V_0} \equiv T + T_0, \quad (1.2.3)$$

where the new temperatures T and T_0 are defined as shown. Thus, the intercept of the straight line generated by extrapolation from the two fixed points of 0 and 100°C (that is, the value τ at which V would vanish on that straight line if *He* could be maintained as an ideal gas to ultralow temperatures⁵) occurs when $T_0 \equiv -100V_0/(V_{100} - V_0) = -273.15^\circ\text{C}$. This suggests a natural lower limit to temperature, namely, the point where V so constructed vanishes. It also suggests a shift of scale whereby the quantity $T = 100V/(V_{100} - V_0)$ is the fundamental entity of interest. Adoption of this approach leads an absolute scale for quantifying hotness levels; we use as the appropriate temperature unit the *thermodynamic temperature scale* $T(\text{K}) = \tau(^{\circ}\text{C}) + 273.15$, where K stands for *kelvins*. This still maintains the desired proportionality between absolute temperature and measured volumes of *He* at fixed, low pressures.

Clearly, one could alternatively have used changes in pressure of an ideal gas maintained at a constant volume as a measure of empirical temperature, so long as the pressure remains in a range where ideality obtains. In that case, at constant volume, one would set up the scale as (with an obvious subscript notation)

$$\tau = 100(P - P_0)/(P_{100} - P_0) = 100P/(P_{100} - P_0) - 100P_0/(P_{100} - P_0) \equiv T + T_0. \quad (1.2.4)$$

Here the intercept of the straight line generated by measurements at P_{100} and P_0 occurs at the value $\tau = -273.15^\circ\text{C}$ where P would vanish if the ideal gas state could be maintained at all temperatures.

Again, setting up a linear absolute temperature scales through pressure measurements at constant volume is an obvious next step.

Obviously, the introduction of the concept of an ideal gas is only an idealization of what can actually be achieved in practice. On the more practical side, one might, for example, carry out volumetric measurements of N_2 gas as a function of temperature in the range $+100$ to -100 °C, while maintaining a constant pressure at 1, 2, 3 bar, and so on. One obtains a linear plot at each pressure, with a slope that increases with pressure. However, all such lines *extrapolate* to a common value very close to -273 °C at zero volume.

At a more fundamental level, one needs to ask whether a temperature scale tied to a particular set of substances is actually of fundamental significance. The answer is provided in Section 2.4, where we show that the absolute scale is independent of what is chosen as a working substance.

Use of Triple Point

A better absolute standard is provided by the so-called *triple point of water*. As shown later,⁴ the coexistence conditions of water in the solid, liquid, and vapor state can occur only under a set of precisely controlled, invariant conditions, determined by the physical characteristics of H_2O , that are completely reproducible all over the world. For consistency with the above absolute temperature scheme, the triple point of water in equilibrium with both steam and ice at a pressure of 4.585 Torr is assigned a temperature $T(\text{triple point of H}_2\text{O}) = 273.16 \text{ K} \equiv T_t$. Then any other absolute temperature is determined through the proportionality $T = (P/P_t) \times 273.16$, where P is the pressure at T , and P_t is the pressure measured for He in equilibrium with water at its triple point.

The use of gas thermometers tends to be awkward. One can use more convenient measurement by calibrating other thermometers against the He gas thermometer in the range of hotness levels where these two overlap. The new system is so chosen that its range of operation extends over temperatures where use of the gas thermometer is awkward or impossible. Such a calibrated unit may be used in turn to calibrate yet another system over their common range of hotness levels; the third system is selected so as to extend the measurements over another range of hotness levels that remained inaccessible to the secondary equipment. The process can be systematically extended to both higher and lower ranges of hotness levels. Details of the requisite procedures, beyond the purview of the present discussion, are provided by many sources of information in the literature.³

Additional Information

- 1.2.1. The zeroth law has been stated in a variety of different ways, many of which hinge on the observation that heat does not move spontaneously from a colder to a hotter body. Such a declaration involves the concept of heat that is introduced only much later; also, such a statement is closely tied to the second law, introduced only much later. The present discussion is more general and avoids these difficulties.
- 1.2.2. H.A. Buchdahl, *The Concepts of Classical Thermodynamics* (Cambridge University Press, 1966), Chap. 2.
- 1.2.3. A very comprehensive account may be found in *Temperature, its Measurement and Control in Science and Industry*, American Institute of Physics, New York, which is a multiauthor, multivolume compendium.

- 1.2.4.** In Section 2.3, it will be shown that when two phases of a pure material (e.g., water and steam) are maintained in equilibrium at a fixed pressure, the temperature of the system remains fixed. Similarly, it will be shown that three such phases (e.g., ice, water, and steam) can coexist only at one particular pressure and temperature, termed the *triple point*.
- 1.2.5.** According to the third law of thermodynamics, taken up later, the ideal gas concept fails at lower achievable temperatures; no material remains in the (ideal) gaseous state for all possible τ . This fact, however, does not deter us from carrying out an extrapolation that indicates at what value of τ , the volume of an ideal gas would vanish if such a gas could be maintained at all temperatures.

1.3 Mathematical Apparatus

We now turn to a summary of mathematical operations that must be properly mastered before we can deal with the thermodynamic principles discussed later. So, be patient. Forget about familiar material, but review or learn what is not familiar. Your particular attention is directed to the discussion of exact differentials; these play a central role in our further development.

Transformation of Variables

The method of transformation of variables in three dimensions can readily be generalized to higher dimensions. Let $F(x,y,z)$ be some function of the three independent variables (in thermodynamics, these usually are not spatial coordinates, but thermodynamic coordinates), each of which may be rewritten in terms of three different independent variables u,v,w that happen to be more convenient for the description of phenomena of interest. We write these interrelations as $x = x(u,v,w)$, $y = y(u,v,w)$, and $z = z(u,v,w)$, so that in terms of the new variables, the original function becomes

$$F(x, y, z) = F[x(u, v, w), y(u, v, w), z(u, v, w)] = G(u, v, w) \equiv F(u, v, w). \quad (1.3.1)$$

As indicated here, in changing coordinates from (x,y,z) to (u,v,w) , the original function F assumes a different functional form, G . However, to avoid profusion of symbols and confusion in interpretation, the same symbol is customarily maintained for both functions. This reflects the fact that the physical interpretation of the mathematical formulation remains unaltered by any transformation of coordinate representation.

On differentiation of Eq. (1.3.1) with respect to u and invoking the chain rule of differentiation, one obtains

$$\left(\frac{\partial F}{\partial u}\right)_{v,w} = \left(\frac{\partial F}{\partial x}\right)_{y,z} \left(\frac{\partial x}{\partial u}\right)_{v,w} + \left(\frac{\partial F}{\partial y}\right)_{x,z} \left(\frac{\partial y}{\partial u}\right)_{v,w} + \left(\frac{\partial F}{\partial z}\right)_{x,y} \left(\frac{\partial z}{\partial u}\right)_{v,w}, \quad (1.3.2)$$

with similar expressions for $(\partial F/\partial v)$ and $(\partial F/\partial w)$.

For comparison, we now cite the total differential of the original analytic function $F(x,y,z)$ as

$$dF = \left(\frac{\partial F}{\partial x}\right)_{y,z} dx + \left(\frac{\partial F}{\partial y}\right)_{x,z} dy + \left(\frac{\partial F}{\partial z}\right)_{x,y} dz, \quad (1.3.3)$$

which we next abbreviate as

$$dF \equiv Xdx + Ydy + Zdz, \quad (1.3.4)$$

with $X = (\partial F/\partial x)_{y,z}$, $Y = (\partial F/\partial y)_{x,z}$, $Z = (\partial F/\partial z)_{x,y}$. Then, on replacing the partial F derivatives in Eq. (1.3.2) with X , Y , and Z , one obtains

$$\left(\frac{\partial F}{\partial u}\right)_{v,w} = X\left(\frac{\partial x}{\partial u}\right)_{v,w} + Y\left(\frac{\partial y}{\partial u}\right)_{v,w} + Z\left(\frac{\partial z}{\partial u}\right)_{v,w}. \quad (1.3.5)$$

Thus, it appears as if on differentiating F in Eq. (1.3.4) with respect to u to obtain Eq. (1.3.5), we had left the coefficients X , Y , and Z unaltered and “differentiated” solely dx , dy , and dz . However, Eq. (1.3.5) is equivalent to Eq. (1.3.2), which resolves the apparent puzzle.

Partial Derivatives with Different Constraints

As a special case of the above, we set $u \equiv x$ and restrict ourselves to two independent variables, discarding z and w . Equation (1.3.2) then reduces to

$$\left(\frac{\partial F}{\partial x}\right)_v = \left(\frac{\partial F}{\partial x}\right)_y + \left(\frac{\partial F}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_v. \quad (1.3.6)$$

The above is a powerful tool that finds application when it is difficult or impossible to measure the quantity $(\partial F/\partial x)_v$ at constant v , while the specification of $(\partial F/\partial x)_y$ is experimentally feasible. Obviously, it must also be necessary to experimentally determine or to look up in tabulations the partial derivatives $(\partial F/\partial y)_x$ and $(\partial y/\partial x)_v$.

Often one deals with situations where a particular function of two variables is found to be a constant: C , whence $F(x,y) = C$. It immediately follows that x and y cannot be independent: we may thus solve for $y = y(x)$ to write $dy = (\partial y/\partial x)_F dx$, so that

$$dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_F dx = 0. \quad (1.3.7)$$

This leads to another useful result of importance, namely

$$\left(\frac{\partial y}{\partial x}\right)_F = -\frac{(\partial F/\partial x)_y}{(\partial F/\partial y)_x}. \quad (1.3.8)$$

Here a partial derivative that may be hard to evaluate with F fixed is rewritten in terms of partial derivatives involving F that may be much easier to determine. Many cases of this type will be encountered later.

We next solve $F(x,y) = C$ for $x = x(y)$; by the same steps, this leads to the result

$$\left(\frac{\partial x}{\partial y}\right)_F = -\frac{(\partial F/\partial y)_x}{(\partial F/\partial x)_y}. \quad (1.3.9)$$

Comparison of these two expressions yields the *reciprocal theorem*:

$$(\partial x/\partial y)_F = 1/[(\partial y/\partial x)_F], \quad (1.3.10)$$

which is extremely useful when it is difficult to deal with a function x expressed in terms of y , but when it is easy to handle y expressed in terms of x . Note the requirement that F be held fixed.

If F is a function of three independent variables and when $F(x,y,z) = C$, a constant, only two of the variables are independent. Solve for $x = x(y,z)$ or $y = y(x,z)$, so that

$$dx = (\partial x / \partial y)_{z,F} dy + (\partial x / \partial z)_{y,F} dz \quad (1.3.11a)$$

$$dy = (\partial y / \partial x)_{z,F} dx + (\partial y / \partial z)_{x,F} dz. \quad (1.3.11b)$$

Substitute the second expression into the first and collect terms to find

$$\left[1 - (\partial x / \partial y)_{z,F} (\partial y / \partial x)_{z,F}\right] dx = \left[(\partial x / \partial y)_{z,F} (\partial y / \partial z)_{x,F} + (\partial x / \partial z)_{y,F}\right] dz. \quad (1.3.12)$$

On account of Eq. (1.3.10), the left-hand side vanishes, and the right-hand side may be rewritten in the form of the *reciprocity theorem*,

$$(\partial x / \partial y)_{z,F} (\partial y / \partial z)_{x,F} (\partial z / \partial x)_{y,F} = -1, \quad (1.3.13)$$

which is useful in specialty applications.

Yet another relation is found when $F(x,y) = C$, where C is a constant, and on expressing x and y in terms of two other independent variables, u and v . Set $x = x(u,v)$ and $y = y(u,v)$; by the chain rule of differentiation,

$$(\partial F / \partial u)_v = 0 = (\partial F / \partial x)_y (\partial x / \partial u)_{v,F} + (\partial F / \partial y)_x (\partial y / \partial u)_{v,F}, \quad (1.3.14)$$

which may be rearranged as

$$\frac{(\partial y / \partial u)_{v,F}}{(\partial x / \partial u)_{v,F}} = -\frac{(\partial F / \partial x)_y}{(\partial F / \partial y)_x}. \quad (1.3.15)$$

On now introducing Eq. (1.3.8), one obtains finally

$$\left(\frac{\partial y}{\partial x}\right) = \frac{(\partial y / \partial u)_{v,F}}{(\partial x / \partial u)_{v,F}}, \quad (1.3.16)$$

which is useful in cases where the derivative on the left is not readily evaluated, but those on the right are easily determined.

Euler's Theorem of Homogeneous Functions

A theorem of great importance in thermodynamics is based on a thought experiment: Consider a system containing n_1 moles of species 1, n_2 moles of species 2, ..., n_r moles of species r . On doubling all moles numbers at constant pressure and temperature, the volume of this system also doubles. A number of thermodynamic entities exhibit such a property, whereby a change of all variables (as opposed to the parameters; see below) by a given factor also changes the thermodynamic function by this same factor. To examine the consequences, consider function $F(x_1, x_2, \dots, x_r)$, for which $dF = F'_1 dx_1 + F'_2 dx_2 + \dots + F'_r dx_r$, where the primes indicate partial derivatives. Then change all independent variables proportionally to their original values, using a common factor $d\lambda$, so that

$dx_i = x_i d\lambda$ for all i , and require a proportional change in F , such that $dF = F d\lambda$. Then we note that $F d\lambda = \sum_i F'_i x_i d\lambda$, from which we obtain

$$F(x_1, x_2, \dots, x_r) = \sum_{i=1}^r \quad (1.3.17)$$

This relationship is known as *Euler's theorem for homogeneous functions of degree one*. This is a theorem of great importance in thermodynamics, as will become evident later.

In addition to the dependence on the x_i , the function F may also display a dependence on parameters such as pressure P or temperature T —quantities that remain unaltered in the above manipulations. However, such parameters may assume different values under different experimental conditions. Hence, partial derivatives of $F = F(T, P, x_1, x_2, \dots, x_r)$, taken with respect to parameters (here T or P at constant x_i), are mathematically appropriate.

Exact Differentials

We now turn to another fundamental concept of great importance. For a system characterized by thermodynamic variables x_1, x_2, \dots, x_r , we will have many occasions to examine differentials such as

$$dL \equiv \sum_i X_i(x_1, x_2, \dots, x_r) dx_i, \quad (1.3.18)$$

which *look* like the differential of a function L . However, the d symbol is specifically designed to indicate that the increment in L and hence, the integral $\int dL$, depends on the particular path that is taken. For example, the energy I expend in going from point A to point B , depends on whether I slide over an icy surface or wade through muddy terrain, or run up and down a series of staircases. To handle such different situations, it is necessary that every x_j be specified by the particular sequence of values it assumes, as I (more generally, the system) proceed(s) along the chosen path from a given initial state (L_i) to a given final state (L_f). The sequence of steps might, for example, be specified by indicating the position I am in as time t progresses. Then, a change in path alters the indicated differential form and the related integral. Differentials of this type are known as *Pfaffian forms*; here, dL is simply a short-hand symbol for the sum on the right, nothing more.

Working with functions of this type is clearly awkward and ought, if at all possible, to be avoided. In thermodynamics, great emphasis is therefore placed on finding a special class of functions, $R(x_1, x_2, \dots, x_r)$, that, when integrated, depend solely on the initial and final states of the system; stated differently, they are independent of the particular path by which the system proceeds. The differential of this special class of functions is unique:

$$dR = \sum_{i=1}^r \left(\frac{\partial R}{\partial x_i} \right)_{x_j \neq i} dx_i \equiv \sum_{i=1}^r X_i dx_i. \quad (1.3.19)$$

Note in particular that in this case, all the coefficients X_i may be obtained by differentiation of the single function $R(x_1, x_2, \dots, x_r)$.

Such a mathematical entity is known as a *function of state of the system* and its differential dR is known as an *exact differential*. A theorem provided by *Carathéodory* (Chapter 9) specifies conditions under which Pfaffians of the form (1.3.18) can be converted to functions of state by the introduction of an *integrating denominator* λ , such that $dR = dL/\lambda$. This conversion is of particular importance in conjunction with the formulation of the second law of thermodynamics, and will be discussed further in Section 1.8.

Functions of state in class R are subject to the following requirements:

1. R is a real, single-valued, analytic function of the thermodynamic variables that characterize the state of a system.¹
2. The difference in R for a system in two different states depends solely on these two states, not on the path chosen to connect these two states.
3. The change in R for a cyclic process is identically zero.
4. The quantity dR is an exact differential which has the form of Eq. (1.3.19).

Elements of Vector Analysis

We briefly review here several pertinent elements of vector analysis; for a better and more complete description, the reader is referred to relevant textbooks. Examples of vectors are the position vector $\mathbf{r} = ix + jy + kz$, where \mathbf{i}, \mathbf{j} , and \mathbf{k} are the unit vectors that coincide with the mutually orthogonal x , y , and z axes of the coordinate system, respectively, and x , y , and z are the corresponding coordinate values. A vector in this space is designated by $\mathbf{A} = iA_x + jA_y + kA_z$, where the A_λ are the components of the \mathbf{A} vector along the three axes. We will also encounter the *gradient vector operator*, defined by $\nabla \equiv i\partial/\partial x + j\partial/\partial y + k\partial/\partial z$.

The following vector manipulations are of relevance:

- (i) The *dot product* of two vectors,

$$\mathbf{A} \cdot \mathbf{B} = |\mathbf{A}||\mathbf{B}|\cos \theta_{AB}, \quad (1.3.20)$$

where $|\mathbf{A}|$ is the magnitude of the vector \mathbf{A} , and where θ_{AB} is the angle between the vectors in the plane defined by them. Clearly, by definition, the dot product results in the formation of a scalar. Since \mathbf{i}, \mathbf{j} , and \mathbf{k} are orthonormal, it follows that $\mathbf{i} \cdot \mathbf{i} = \mathbf{j} \cdot \mathbf{j} = \mathbf{k} \cdot \mathbf{k} = 1$ and $\mathbf{e}_\lambda \cdot \mathbf{e}_\mu = 0$, with $\lambda \neq \mu$ and $\mathbf{e}_\lambda = \mathbf{i}, \mathbf{j}, \mathbf{k}$. Thus the dot product of two vectors is given by

$$\mathbf{A} \cdot \mathbf{B} = (iA_x + jA_y + kA_z) \cdot (iB_x + jB_y + kB_z) = A_xB_x + A_yB_y + A_zB_z \quad (1.3.21)$$

It is easily checked that the operation is *commutative*, $\mathbf{A} \cdot \mathbf{B} = \mathbf{B} \cdot \mathbf{A}$, and *distributive*, $\mathbf{A} \cdot (\mathbf{B} + \mathbf{C}) = \mathbf{A} \cdot \mathbf{B} + \mathbf{A} \cdot \mathbf{C}$.

Another operation of importance involves the gradient vector dot product:

$$\nabla \cdot \mathbf{A} = (i\partial/\partial x + j\partial/\partial y + k\partial/\partial z) \cdot (iA_x + jA_y + kA_z) = \frac{\partial A_x}{\partial x} + \frac{\partial A_y}{\partial y} + \frac{\partial A_z}{\partial z}. \quad (1.3.22)$$

This operation is called the *divergence*; it measures the degree to which the vector \mathbf{A} spreads out from any given point. For, along a given direction x , a change in distance dx entails a change of the vector from $iA_x(x)$ to $iA_x(x + dx) \approx i[A_x(x) + (\partial A_x/\partial x)dx]$, in which the partial derivative in the last term specifies the rate of increase or decrease of the vector along the positive x direction. Equation (1.3.22) then clearly represents the three-dimensional counterpart.

- (ii) Another useful entity is the *cross-product* of two vectors as defined by

$$\mathbf{A} \times \mathbf{B} = \check{n}|\mathbf{A}||\mathbf{B}|\sin \theta_{AB}. \quad (1.3.23)$$

Here \check{n} is the unit vector perpendicular to the plane defined by \mathbf{A} and \mathbf{B} . It points in the direction specified by the right-hand rule. In light of their definitions, the orthonormal unit vectors satisfy the relations $\mathbf{e}_\lambda \times \mathbf{e}_\lambda = 0$, and $(\mathbf{i} \times \mathbf{j}) = \mathbf{k} = -(\mathbf{j} \times \mathbf{i})$; $(\mathbf{j} \times \mathbf{k}) = \mathbf{i} = -(\mathbf{k} \times \mathbf{j})$; $(\mathbf{k} \times \mathbf{i}) = \mathbf{j} = -(\mathbf{i} \times \mathbf{k})$. With

these rules, it is readily checked that $\mathbf{A} \times \mathbf{B} = (iA_x + jA_y + kA_z) \times (iB_x + jB_y + kB_z) = -(\mathbf{B} \times \mathbf{A})$ and that this cross-product may be recast in determinantal form as

$$\mathbf{A} \times \mathbf{B} = \begin{bmatrix} i & j & k \\ A_x & A_y & A_z \\ B_x & B_y & B_z \end{bmatrix}. \quad (1.3.24)$$

The cross-product obeys anticommutation rules.

Similar rules apply to the gradient vector; we obtain

$$\nabla \times \mathbf{A} = \begin{vmatrix} i & j & k \\ \partial/\partial x & \partial/\partial y & \partial/\partial z \\ A_x & A_y & A_z \end{vmatrix}, \quad (1.3.25a)$$

which may be expanded as

$$\nabla \times \mathbf{A} = i \left(\frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \right) + j \left(\frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right) + k \left(\frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right). \quad (1.3.25b)$$

The operation (1.3.25) is termed the *curl*; the name is appropriate because the curl of a vector that points in a fixed direction vanishes, whereas a vector that curves around a fixed axis has a large value associated with it.

Last, we cite the relation for the volume of a parallelepiped which generally may be nonorthogonal. If \mathbf{A} , \mathbf{B} , and \mathbf{C} represent the vectors of length A , B , and C along the tilted x , y , and z axes of the parallelepiped, the volume within this figure is given by

$$V = (\mathbf{A} \times \mathbf{B}) \cdot \mathbf{C}. \quad (1.3.25c)$$

We call attention to several more involved vector operations listed in Table 1.3.I. These may be verified by writing out both sides of each equation in component form.

Table 1.3.I

Selected vector operations

$$\mathbf{A} \cdot (\mathbf{B} \times \mathbf{C}) = \mathbf{B} \cdot (\mathbf{C} \times \mathbf{A}) = \mathbf{C} \cdot (\mathbf{A} \times \mathbf{B}) \quad (a)$$

$$\mathbf{A} \times (\mathbf{B} \times \mathbf{C}) = \mathbf{B}(\mathbf{A} \cdot \mathbf{C}) - \mathbf{C}(\mathbf{A} \cdot \mathbf{B}) \quad (b)$$

$$\nabla(fg) = f\nabla g + g\nabla f \quad (c)$$

$$\nabla \cdot (f\mathbf{A}) = f(\nabla \cdot \mathbf{A}) + \mathbf{A} \cdot (\nabla f) \quad (d)$$

$$\nabla \times (f\mathbf{A}) = f(\nabla \times \mathbf{A}) - \mathbf{A} \times (\nabla f) \quad (e)$$

$$\nabla \cdot (\mathbf{A} \times \mathbf{B}) = \mathbf{B} \cdot (\nabla \times \mathbf{A}) - \mathbf{A} \cdot (\nabla \times \mathbf{B}) \quad (f)$$

$$\nabla \times (\nabla f) = 0 \quad (g)$$

$$\nabla \times (\nabla \times \mathbf{A}) = \nabla(\nabla \cdot \mathbf{A}) - \nabla \cdot (\nabla \mathbf{A}) \quad (h)$$

$$\nabla \cdot (\nabla \times \mathbf{A}) = 0 \quad (i)$$

Selected Integral Operations

$$\int_i^f \nabla \phi \cdot d\mathbf{r} = \phi(f) - \phi(i) \quad \text{Gradient theorem} \quad (j)$$

$$\iiint_V \nabla \cdot \mathbf{A} d^3r = \iint_S \mathbf{A} \cdot \mathbf{\hat{n}} d^2r \quad \text{Gauss theorem} \quad (k)$$

$$\iint_S (\nabla \times \mathbf{A}) \cdot d^2\mathbf{r} = \oint \mathbf{A} \cdot d\mathbf{r} \quad \text{Stokes theorem} \quad (l)$$

Remarks: \mathbf{A} , \mathbf{B} , and \mathbf{C} are the vector quantities, $\hat{\mathbf{n}}$ is the outer unit normal to a surface element, g, f , and ϕ are the scalar quantities. The integral in (j) is a *line integral* connecting an initial to a final state; the ones to the left and right of (k) extend over the volume and over the surface of a body; the ones to the left and right of (l) extend over the surface and form a closed loop on the surface of a body.

For mathematical proofs of the above relations, one must consult any text on vector theory; for assistance and general guidance, a simplified rationalization is provided in the Appendix, below.

First-Order Differential Equations

We shall have occasion to deal with a first-order differential equation of the form

$$dy(x)/dx + R(x)y(x) = X(x). \quad (1.3.26)$$

Its solution, as may be checked by direct substitution, is given by

$$y(x) = \gamma(x)^{-1} \left[\int dx \gamma(x) X(x) + C \right], \quad (1.3.27a)$$

where

$$\gamma(x) \equiv \exp \left[\int dx R(x) \right], \quad (1.3.27b)$$

and where C is an arbitrary constant.

Integrals with Variable Limits

On occasion, we will handle cases where differentials or derivatives must be taken of integrals with variable limits. Three such situations are of importance:

- (i) The first is of the type (V is the volume of the system and L is a variable length of the system along a particular axis)

$$P = - \frac{\partial}{\partial V} \left[\iiint dx dy dz f(x, y, z; V, Y) \right]_Y, \quad (1.3.28)$$

in which the function f depends on the x, y, z distance coordinates which remain within the limits $-L/2 \leq x, y, z \leq L/2$, where L is the length of a cube of volume $V = L^3$, equivalent to the actual volume of the system.^{2,3} Y is a parameter in the problem, such as temperature, pressure, or magnetic field. Since the limits of the integral, as well as the integrand itself, are variable, one cannot simply interchange the integral and differential operators. To deal with this case, we introduce fractional coordinates $\xi \equiv x/L$, $\eta \equiv y/L$, $\zeta \equiv z/L$, in the fixed range $-1/2 \leq \xi, \eta, \zeta \leq 1/2$, and we set $dx dy dz = L^3 d\xi d\eta d\zeta$, whence

$$\partial/\partial V = (\partial/\partial L)(\partial L/\partial V) = \left(3V^{2/3}\right)^{-1} (\partial/\partial L) = (1/3L^2)(\partial/\partial L). \quad (1.3.29)$$

Thus, we obtain

$$P = - \frac{1}{3L^2} \frac{\partial}{\partial L} \left[\int_{-1/2}^{1/2} \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} d\xi d\eta d\zeta L^3 f(\xi, \eta, \zeta; L, Y) \right]_Y. \quad (1.3.30)$$

With the limits on the integral now fixed, one may place the partial derivative inside the integral sign, whereby

$$P = - \iiint d\xi d\eta d\zeta f(\xi, \eta, \zeta; L, Y) - \frac{L}{3} \iiint d\xi d\eta d\zeta \frac{\partial f(\xi, \eta, \zeta; L, Y)}{\partial L} \Big|_Y. \quad (1.3.31)$$

Finally, transform back to the original variables:

$$P = -\frac{1}{L^3} \iiint dxdydz f(x, y, z; V, Y) - \frac{1}{3L^2} \iiint dxdydz \left(\frac{\partial f}{\partial V} \right) \Big|_Y \frac{dV}{dL}, \quad (1.3.32)$$

which may be put in the final form

$$P = -\frac{1}{V} \int dxdydz f(x, y, z; V, Y) - \int dxdydz \frac{\partial f}{\partial V} \Big|_Y. \quad (1.3.33)$$

(ii) Another operation of interest is of the type

$$\left(\frac{\partial I}{\partial Y} \right)_Z \equiv \left[\frac{\partial}{\partial Y} \int_{V(Y,Z)} dxdydz g(x, y, z; Y, Z) \right]_Z, \quad (1.3.34)$$

in which the integration limits themselves depend on the variable of the differentiation. Again, we use the method of fractional coordinates to write

$$\begin{aligned} \left(\frac{\partial I}{\partial Y} \right)_Z &= \frac{\partial}{\partial Y} \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} d\xi d\eta d\zeta L^3 g(\xi, \eta, \zeta; Y, Z) \Big|_Z \\ &= \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} d\xi d\eta d\zeta \frac{\partial}{\partial Y} [Vg(\xi, \eta, \zeta; Y, Z)] \Big|_Z \\ &= \int_V dxdydz \frac{\partial g(x, y, z; Y, Z)}{\partial Y} \Big|_Z + \int_V dxdydz \left[\frac{g(x, y, z; Y, Z)}{V(Y, Z)} \right] \left(\frac{\partial V(Y, Z)}{\partial Y} \right) \Big|_Z. \end{aligned} \quad (1.3.35)$$

(iii) Last, in later discussion, it will be necessary to consider the differential of the integral $\int_V d^3\mathbf{r}(\mathbf{M} \cdot \mathbf{H})$, that is encountered in the study of magnetic effects. We treat this quantity as shown below:

$$\begin{aligned} d \int_V dxdydz (\mathbf{M} \cdot \mathbf{H}) &= d \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} d\xi d\eta d\zeta (\mathbf{M} \cdot \mathbf{H}) V \\ &= \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} d\xi d\eta d\zeta d[V(\mathbf{M} \cdot \mathbf{H})] = \int_V dxdydz (1/V) d[V(\mathbf{M} \cdot \mathbf{H})] \\ &= \int_V d^3\mathbf{r} [\mathbf{M} \cdot \mathbf{H} / V] dV + \int_V d^3\mathbf{r} \mathbf{H} \cdot d\mathbf{M} + \int_V d^3\mathbf{r} \mathbf{M} \cdot d\mathbf{H}. \end{aligned} \quad (1.3.36)$$

Appendix: Rationalization of Integral Theorems

We introduce a heuristic (in common parlance, a hand waving) argument to rationalize the various integral theorems. Line (j) is an elementary consequence for the definition of a differential quantity under an integral sign. As to line (k), consider a one-dimensional flow of incompressible matter along

x , and compare the mass m per unit volume of fluid at x and at $x + dx$. Then set $m(x + dx) = m(x) + (\partial m / \partial x)dx$, where the second term indicates the net accumulation or depletion of m as the material traverses the distance dx . In three dimensions, this generalizes to $(\partial m / \partial x)dx + (\partial m / \partial y)dy + (\partial m / \partial z)dz = \nabla m \cdot d^3\mathbf{r}$. The integral on the left of line (k) thus represents the net accumulation (or depletion) of material within the volume, brought about by the balance between influx and outflow across the boundaries of the system. The right side represents the additive effect of summing the transfer of mass patchwise across the entire surface. The operation $\tilde{\mathbf{n}} \cdot d^2\mathbf{r}$ ensures that only the transfer of m in the direction orthogonal to each patch of size $d^2\mathbf{r}$ is credited to the total accumulation (or depletion). The minus sign is needed since in the process of accumulation account must be taken of the fact that $\tilde{\mathbf{n}}$ points in the direction away from the interior of the body. The integration sums the contributions from each patch.

A heuristic treatment of the curl operation is based on the attached Figure 1.3.1, which shows the counterclockwise circulation of a vector quantity \mathbf{V} inside a rectangular two-dimensional unit in the x - y plane. The circulation $C = \oint \mathbf{V} \cdot d\mathbf{l} = \oint [(iV_x + jV_y) \cdot (i dx + j dy)] = \int V_x dx + \int V_y dy$ consists of the following four branches. from x_0, y_0 to $x_0 + dx, y_0$ along 1, involving V_x ; here y_0 is fixed. To first order in smallness along dx , $V_x(x, y)$ may be replaced by its average (constant) value $V_x(x_0, y_0)$; over the distance dx , one incurs the contribution $V_x(x_0, y_0)dx$. From $x_0 + dx, y_0$ to $x_0 + dx, y_0 + dy$ along 2, involving V_y ; here $x_0 + dx$ remains fixed. To first order in smallness, we replace V_y with its average to obtain $V_y(x_0 + dx, y_0)dy$. We next expand the multiplier in a first-order Taylor series: $V_y(x_0 + dx, y_0) = V_y(x_0, y_0) + (\partial V_y / \partial x)dx$, so that the resultant along 2 reads $[V_y(x_0, y_0) + (\partial V_y / \partial x)dx]dy$. The remaining branches are handled in a similar manner: along 3, we obtain the contribution $[V_x(x_0, y_0) + (\partial V_x / \partial y)dy](-dx)$; along 4, we obtain $V_y(x_0, y_0)(-dy)$. On summing, the averages drop out and the above contributions add up to

$$C = [(\partial V_y / \partial x) - (\partial V_x / \partial y)] dA_z, \quad (1.3.37)$$

where $dA_z = dxdy$ is the surface area element perpendicular to the z direction. The curl is thus seen to be related to the vortex-like circulation of a fluid within an elementary cell.

Similar results are found along the yz and xz planes, by cyclic permutation of the subscripts. The three-dimensional analog of $C/dxdy$ reads

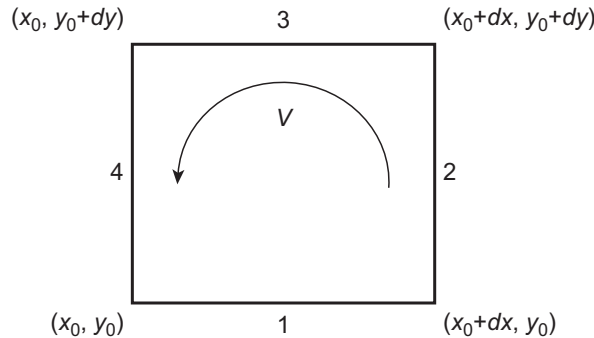


FIGURE 1.3.1

Illustration depicting the curl operation.

$$\nabla \times \mathbf{V} \equiv \mathbf{i}[(\partial V_z/\partial y) - (\partial V_y/\partial z)] + \mathbf{j}[(\partial V_x/\partial z) - (\partial V_z/\partial x)] + \mathbf{k}[(\partial V_y/\partial x) - (\partial V_x/\partial y)], \quad (1.3.38)$$

where the left-hand side is the conventional abbreviation for the curl operation. A short-hand notation for the above left-hand side is given by the determinant (1.3.25a).

Stokes' theorem is rationalized by considering a surface that consists of an assembly of elementary cells of which a portion is shown in Figure 1.3.2. In the interior, the effects of the various current whirls cancel each other out, but this is not the case for the elementary units terminating on the exterior line that delineates (constitutes) the surface. These exterior elements join to form a continuous closed loop for the boundary to the surface.

The three-dimensional analog of Eq. (1.17.1) over the entire surface reads

$$\iint \nabla \times \mathbf{V} \cdot d\boldsymbol{\sigma} = \int \{ \mathbf{i}[(\partial V_z/\partial y) - (\partial V_y/\partial z)] + \mathbf{j}[(\partial V_x/\partial z) - (\partial V_z/\partial x)] + \mathbf{k}[(\partial V_y/\partial x) - (\partial V_x/\partial y)] \} \cdot [\mathbf{i}dA_x + \mathbf{j}dA_y + \mathbf{k}dA_z], \quad (1.3.39)$$

and the line integral along the perimeter is of the form

$$\int_0 \mathbf{V} \cdot d\mathbf{l} = \int_0 [(iV_x + jV_y + kV_z) \cdot (idx + jdy + kdz)], \quad (1.3.40)$$

where the 0 subscript denotes the fact that the line integral over the perimeter must be closed on itself. We have thus rationalized the Stokes' theorem:

$$\iint \nabla \times \mathbf{V} \cdot d\boldsymbol{\sigma} = \int_0 \mathbf{V} \cdot d\mathbf{l}. \quad (1.3.41)$$

Gaussian Integrals

In later chapters, we need to perform integrations that involve the function

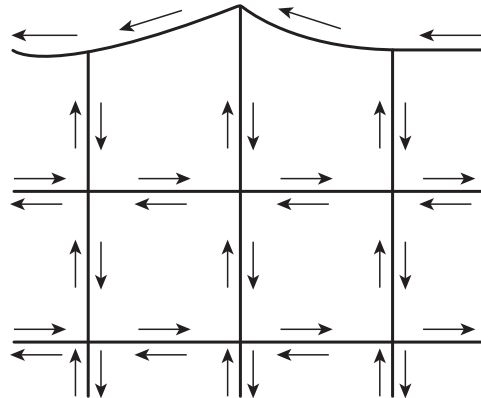


FIGURE 1.3.2

Illustration depicting the Stokes operation.

$$f(t) = \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2 t^2}, \quad (1.3.42a)$$

i.e., we wish to determine

$$A = \int_{-\infty}^{\infty} dt \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2 t^2}, \quad (1.3.42b)$$

where α is a constant. Now set $x = \alpha t$, whence $A = (1/\sqrt{\pi}) \int_{-\infty}^{\infty} dx e^{-x^2}$. We then introduce a neat trick: we determine, instead, the square of the above area as

$$A^2 = (\pi)^{-1} \int_{-\infty}^{\infty} dx e^{-x^2} \int_{-\infty}^{\infty} dy e^{-y^2} = (\pi)^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy e^{-(x^2+y^2)}. \quad (1.3.43)$$

Now switch to polar coordinates: $x^2 + y^2 = \rho^2$; $dx dy = \rho d\rho d\theta$, and set $z = e^{-\rho^2}$, so that

$$A^2 = \frac{1}{\pi} \int_0^{\infty} d\rho \rho e^{-\rho^2} \int_0^{2\pi} d\theta = 2 \int_0^{\infty} d\rho \rho e^{-\rho^2} = \int_0^1 dz = 1, \quad (1.3.44a)$$

whence

$$\int_{-\infty}^{\infty} dt \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2 t^2} = 1. \quad (1.3.44b)$$

Note the remarkable fact that this normalization condition is independent of the value of α and that Eq. (1.3.42b) is properly normalized.

Fourier Transform of Gaussians

We also will have occasion to examine the following integral, technically the *Fourier transform* of Eq. (1.3.42a):

$$F(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} dt \frac{\alpha}{\sqrt{\pi}} e^{-\alpha^2 t^2} e^{-i\omega t}. \quad (1.3.45)$$

To handle this integral, we “complete the square” of the exponent of the integrand: set $\alpha^2 t^2 + i\omega t \equiv (\alpha^2 t^2 + i\omega t + \gamma) - \gamma$. Next, represent the quantity in brackets as $(\alpha t + \beta)^2 = \alpha^2 t^2 + 2\alpha\beta t + \beta^2$. This requires setting $\beta^2 = \gamma$ and $\beta = i\omega/2\alpha$, whence $\gamma = -\omega^2/4\alpha^2$. Thus, the Fourier transform of the Gaussian function, Eq. (1.3.45), now reads

$$F(\omega) = \frac{\alpha}{\pi\sqrt{2}} e^{-\omega^2/4\alpha^2} \int_{-\infty}^{\infty} dt e^{-(\alpha t + i\omega/2\alpha)^2}. \quad (1.3.46)$$

This integral may be handled as shown earlier. Set $x = \alpha t + i\omega/2\alpha$, $dx = \alpha dt$. Then

$$F(\omega) = \frac{1}{\pi\sqrt{2}} e^{-\omega^2/4\alpha^2} \int_{-\infty}^{\infty} dx e^{-x^2} = \frac{1}{\sqrt{(2\pi)}} e^{-\omega^2/4\alpha^2}, \quad (1.3.47)$$

where Eq. (1.3.44b) was used. We see then that the Fourier transform of a Gaussian produces another Gaussian function, but one that is not normalized to unity.

Moreover, the evaluation of the integral is of great intrinsic interest. On combining Eqs. (1.3.45) and (1.3.47), we find that

$$\int_{-\infty}^{\infty} dt e^{-\alpha^2 t^2} e^{-i\omega t} = \frac{\sqrt{\pi}}{\alpha} e^{-\omega^2/4\alpha^2}. \quad (1.3.48)$$

The above relation forms one of the cornerstones in statistical mechanics.

Remarks

- 1.3.1.** At isolated singular points, such functions are allowed to be nonanalytic.
- 1.3.2.** A simple method for checking the results shown below is to assume that f is independent of spatial coordinates. In that case, the triple integral of Eq. (1.3.28) may be replaced by $Vf(V, Y)$, so that we obtain $P = -(\partial(Vf)/\partial V)_Y$; the remaining equations simplify correspondingly.
- 1.3.3.** Similar strategies are employed when the solid body is not a simple cube although the mathematical manipulations become more cumbersome. Alternatively, one approximates the actual shape through a juxtaposition of cubes of appropriate sizes that fit into the body, and one then sums the contributions. In any event, the final outcome is not affected by the shape of the body.

1.4 Thermodynamic Forces

One more preliminary discussion! We need to study the concept of thermodynamic forces as presented by Redlich.¹ In this formalism, we posit that changes in a system are brought about by external interventions that require the interaction between the two systems 1 and 2. When initially isolated, the state of each system is characterized by independent deformation coordinates, $\mathbf{x}_1 = \{x_{11}, x_{12}, \dots, x_{1r}\}$ and $\mathbf{x}_2 = \{x_{21}, x_{22}, \dots, x_{2s}\}$. The x_{ij} are entities such as the volume, composition, electric and magnetic polarization, surface area, and similar quantities. As long as the two systems do not interact, all x_{lm} coordinates can assume whatever values are consistent with the physical characteristics of the system. When we now allow the two systems to interact, some of the variables can no longer be altered independently. (This harks back to the discussion of Section 1.2 and anticipates the derivations in Section 2.1). Suppose that during such a process, two deformation coordinates x_{1i} and x_{2j} are simultaneously changed. This interaction may be formally represented by the equation $g(x_{1i}, x_{2j}) = 0$. Nothing prevents us from replacing the variables x_{1i} and x_{2j} by other monotonic varying functions $y_{1i}(x_{1i})$ and

$y_{2j}(x_{2j})$, respectively; this merely alters the mathematical representation, but not the physical characterization, of the interaction. This freedom allows us to select a particular set of coordinates x_{1i} and x_{2j} in such a manner that their differentials for an infinitesimal step in the process obey the relation

$$dx_{1i} + dx_{2j} = 0. \quad (1.4.1)$$

This then gives rise to three possible outcomes while changes dx_{1i} and dx_{2j} are imposed: x_{1i} increases while x_{2j} diminishes, x_{1i} decreases while x_{2j} increases, or x_{1i} and x_{2j} remain unchanged, in which case the universe as a whole remains unchanged. We now set up a quantity $f_{1i}(x_{1i})$ for system 1 and $f_{2j}(x_{2j})$ for system 2, where the f s represent the agents that impose the changes in x_{1i} and in x_{2j} . As a result, three possible outcomes are anticipated, inconformity with Eq. (1.4.1):

$$f_{1i} > f_{2j} \text{ corresponds to } dx_{1i} > 0, \quad dx_{2j} < 0 \quad (1.4.2a)$$

$$f_{1i} < f_{2j} \text{ corresponds to } dx_{1i} < 0, \quad dx_{2j} > 0 \quad (1.4.2b)$$

$$f_{1i} = f_{2j} \text{ corresponds to } dx_{1i} = dx_{2j} = 0. \quad (1.4.2c)$$

The selection of functions for the representation of the various f is arbitrary; one may choose any particular function that can be correlated in a monotonic fashion with each particular deformation coordinate x . This makes it apposite to select particular functions that are convenient in their application. Such selected functions are known as *generalized forces*. For a quantitative scheme that relates numerical values for forces f_{1i} and f_{2j} , with specific numerical values for the two (or more) deformation coordinates x_{1i} and x_{2j} , one applies our freedom of choice. It permits us to select the functional relations that are dictated by the specific physical laws which govern the phenomena of interest. Quantitative measurements also require the calibration of interactions against an accepted standard force appropriate to the measurement under study, again chosen so as to conform to the physical laws that prescribe the interactions.

In succeeding discussions, we frequently associate body 1 with a system of interest and body 2, with the surroundings with which it interacts.

When f_{1i} and f_{2j} differ, processes take place in each system until the equilibrium state $f_{1i} = f_{2j}$ is reached, at which point x_{1i} and x_{2j} become stationary. The fact that processes terminate does not mean that all forces have ceased to exist; rather, they balance each other out.

Reference

1.4.1. O. Redlich, *Rev. Mod. Phys.* **40**, 556 (1968).

1.5 Elements of Work

General Statements

We now turn to the topic of what constitutes work; this information is a prerequisite to what follows. Pay particular attention to the conditions under which work performance depends on the chosen path. Obviously, whenever work is performed irreversibly, the mathematical formulation of work performance does not lead to a function of state.

Work involves the action of a (vector) force \mathbf{f}_i , as defined in Section 1.4, that produces changes in the state of a system by the action of an external agent. For quantitative evaluations, the operation must be performed so that at any stage, the state of the system may be specified by a limited number of independent variables \mathbf{x}_i . The various \mathbf{x}_i components in the listing are known as (*internal*) *thermodynamic coordinates* of the system; the forces \mathbf{f}_i that affect these changes are known as *conjugate thermodynamic coordinates* of the system. In an elemental portion of a given process, such a force brings about a *displacement* $d\mathbf{x}_i$ in the coordinate \mathbf{x}_i . The source of this force is the existence of an external unit—a force reservoir—with which the system interacts. Hence, the need is to consider not only the system itself but also the surroundings within which it operates. It is sometimes stated that quantities capable of external manipulation are *constrained* by experimental conditions.

As indicated below, the extent of work performance of type i can always be either measured or calculated; this permits us to construct a conceptual framework for the thermodynamic properties of a system of interest. In general, \mathbf{f}_i itself depends on \mathbf{x}_i and is not necessarily collinear with it. Then the element of work is specified by the vectorial dot product as $dW = \mathbf{f}(\mathbf{x}_i) \cdot d\mathbf{x}_i$, where the d symbol again indicates that this increment generally involves a path-dependent integral, $\int \mathbf{f}(\mathbf{x}_i) \cdot d\mathbf{x}_i$. Where more than one type of work is performed, the contributions must be summed.

Ordinarily, for purposes of evaluation, the applied force is taken to be small enough that, throughout the entire process, the system deviates only very slightly from prevailing equilibrium conditions. This ensures slow implementation of the process and rules out turbulent or dissipative operations whose description would otherwise require a whole host of extrathermodynamic variables. Nevertheless, we will later take up cases where the applied force does exceed that needed for guaranteeing reversibility.

Under the above conditions, the total work of type i performed on taking a system from state \mathbf{x}_1 to \mathbf{x}_2 is specified by

$$W_i = \int_{\mathbf{x}_1}^{\mathbf{x}_2} \mathbf{f}_i \cdot d\mathbf{x}_i \quad (1.5.1)$$

As explained below, the integral can be rendered path independent if a *potential function* ϕ can be found such that $\mathbf{f} = -\nabla\phi$ (the minus sign is introduced as a universally accepted convention). Aside from this sufficiency condition, other cases will later be cited where a work-related integral is a function of state.

Pressure–Volume Work

We now examine several different types of work performance under quasi-static conditions. We begin with the compression by a piston (cf. Figure 1.5.1) of gas in a cylinder of constant cross-section A . The applied pressure at each stage is only incrementally larger than the opposing gas pressure within the cylinder. With a displacement $-dx$ along the direction of application of the external force, the element of compressive work is specified by

$$dW = f(-dx) = -(f/A)(Adx) = -PdV. \quad (1.5.2)$$

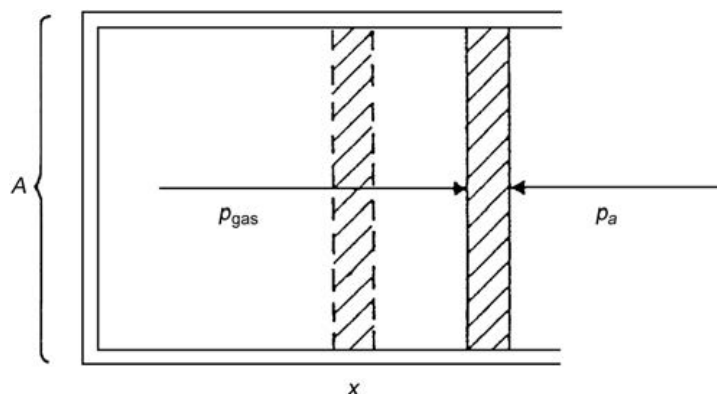


FIGURE 1.5.1

Compression of a gas in a cylinder of constant cross-sectional area A . The volume of the gas is diminished by application of an external pressure.

As a specific simple example, if the contents of the cylinder is an ideal gas, we may write $P = nRT/V$. Then, in a reversible compression, we may set $W = -\int_{V_i}^{V_f} (nRT/V) dV$; if the temperature remains constant, we find

$$W = -(nRT) \int_{V_i}^{V_f} d \ln V = (nRT) \ln(V_i/V_f), \quad (1.5.3a)$$

which is positive since $V_i > V_f$. Thus, work done on the system is represented by a positive quantity. Note that in this particular case, the work performance does depend only on the initial and final values of the volume of the system. At the end of the section, we provide an example where work performance exceeds the constraints of maintaining near equilibrium conditions.

For an irregularly shaped, isotropic object, we let $Pd\sigma$ represent the force acting uniformly on a cross-section element $d\sigma$ of the boundary (Figure 1.5.2), which everywhere recedes uniformly inward by a distance $-dx$ relative to the applied pressure. The element of work is given by

$$dW = -\left(\int_{\sigma} Pd\sigma\right) dx = -PdV, \quad (1.5.3b)$$

as before. However, if the mechanical characteristics of the body are anisotropic, the procedure becomes more complicated; this problem will be taken up in Sections 5.10 and 5.11.

When a thin rod of cross-section A and length l , initially at equilibrium, is stretched or compressed by application of a force f (Figure 1.5.3), it is conventional to introduce a *stress* $\sigma \equiv f/A$ that induces a *strain* $\mathcal{E} \equiv dl/l$ and to set $\sigma > 0 (< 0)$ when the rod is subject to tension (compression); under tension (compression), $dl > 0 (dl < 0)$. Note that in either case, work is performed on the rod. In the elastic limit, when the work element is carried out reversibly,

$$dW = V_0 \sigma d\mathcal{E} \quad (1.5.4)$$

where V_0 is the volume of the unstretched rod. Again, this result must be generalized for anisotropic materials, as shown in Sections 5.10 and 5.11.

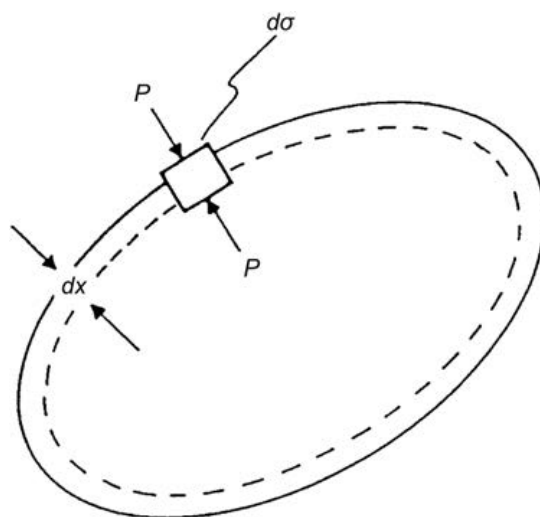


FIGURE 1.5.2

Compression of an irregularly shaped object by application of an external pressure that diminishes the volume.

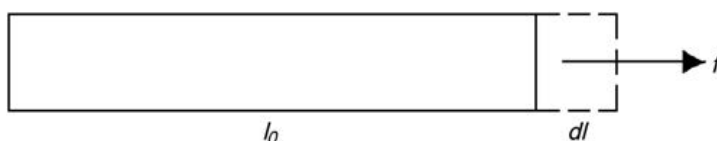


FIGURE 1.5.3

Stretching of a rod by an externally applied force. The length of the bar is increased in this process.

Work in Gravitational Fields

Work done against gravity may be treated in two distinct ways. The first involves material of a constant mass—consisting of n moles of gram atomic mass M —being lifted through a height dz ; the element of work done on the system in this process is

$$\delta W = Mgndz, \quad (1.5.5a)$$

where g is the gravitational constant. In this process, only the potential energy of the system is changed. This operation should be contrasted with incrementing the mass of the body by lifting dn moles to it at height z (relative to a standard height, such as sea level). The work element is then given by

$$\delta W = Mgzdn, \quad (1.5.5b)$$

whereby both the constitution of the system as well as its potential energy have been changed. Which of these two descriptions should be used depends on the process under study.

Work in Electrostatic Fields

A similar situation prevails for a charge q subjected to an electrostatic potential Φ . If the potential is changed in the amount $d\Phi$, the corresponding work is given by $\delta W = qd\Phi$; there is no change in the

thermodynamic deformation coordinates. By contrast, in a process whereby an element of charge dq is taken from infinity (where the potential vanishes) and placed in a location at the electrostatic potential Φ , the element of work is $dW = \Phi dq$. Here, the thermodynamic mass and charge coordinates, as well as the potential energies of the system, are altered.

This latter formulation requires generalization. Let the potential be a function of position, $\Phi = \Phi(\mathbf{r})$, at location \mathbf{r} , where the charge density is given by $\rho(\mathbf{r})$. We increment the charge $d^3\mathbf{r}\rho(\mathbf{r})$ in volume element $d^3\mathbf{r}$ at that location by the amount $dq = d^3\mathbf{r}d\rho(\mathbf{r})$. Then the element of work for bringing the charge increment from infinity to location \mathbf{r} is given by $d^3\mathbf{r}\Phi(\mathbf{r})d\rho(\mathbf{r})$. The work in charging a body of volume V then reads $dW = \int_V d^3\mathbf{r}\Phi(\mathbf{r})d\rho(\mathbf{r})$. Next, introduce Maxwell's equation $\nabla \cdot \mathcal{D} = 4\pi\rho(\mathbf{r})$, where $\rho(\mathbf{r})$ is now the free charge density at location \mathbf{r} , i.e., a charge adjustable by external means and not intrinsic to the medium under study. Here \mathcal{D} is the *electric displacement vector per unit volume*, which is related to the *electric field vector* \mathcal{E} by $\mathcal{D} = \mathcal{E} + 4\pi\mathcal{P}$, in which \mathcal{P} is the *polarization density*. The corresponding change in charge density reads $d\rho = (4\pi)^{-1} \nabla \cdot d\mathcal{D}$. Introduce line (d) of Table 1.3.I, so that we may set

$$dW = \int d^3\mathbf{r}(4\pi)^{-1}(\nabla \cdot d\mathcal{D}\Phi(\mathbf{r})) = (4\pi)^{-1} \int d^3\mathbf{r}[\nabla\Phi \cdot d\mathcal{D} - d\mathcal{D} \cdot \nabla\Phi], \quad (1.5.6a)$$

where the integration involves the entire region of space over which D is present. Gauss' theorem, line (k) of Table 1.3.I, may now be applied to the first of the above two integrals, thus yielding $-(4\pi)^{-1} \int d^2\mathbf{r}\tilde{\mathbf{n}} \cdot \Phi d\mathcal{D}$ where $\tilde{\mathbf{n}}$ is the outer unit normal vector perpendicular to a given surface element. The integration extends over *any arbitrary* surface completely enveloping regions in which the electric displacement field exists. This boundary may therefore be chosen so as to encompass even enormously remote regions where the surface flux vanishes. The first integral may thus be eliminated. In the second, we introduce the electric field vector in terms of the electrostatic potential as $\mathcal{E} = -\nabla\Phi$ so that finally the work element takes the form

$$dW = (4\pi)^{-1} \int d^3\mathbf{r}\mathcal{E} \cdot d\mathcal{D}. \quad (1.5.6b)$$

While appropriate, this expression is not really useful because the integration must be extended over all space. In Section 1.6, we provide an alternative, more useful formulation, namely,

$$dW = - \int_V d^3\mathbf{r}\mathcal{P} \cdot d\mathcal{E}_0, \quad (1.5.6c)$$

in which \mathcal{E}_0 is the applied electric field before introduction of the sample. The polarization vector \mathcal{P} vanishes outside the sample; hence, the integration may be restricted, as indicated, to the sample volume V . In normal operations, the linear relation $\mathcal{P} = \alpha\mathcal{E}$ is applicable, where α is the *electric susceptibility*; alternatively, we set $\mathcal{P} = \alpha_0\mathcal{E}_0$. In specifying Eq. (1.5.6c), we have not taken into account the work required to energize the vacuum in setting up the field \mathcal{E}_0 . This latter quantity, included in the derivations of Section 1.6, normally is of no interest.

Work in Magnetic Fields

The work incurred in subjecting material of volume V to an externally imposed magnetic field \mathcal{H} is given by $dW = V\mathcal{M} \cdot d\mathcal{H}$, where \mathcal{M} is the *magnetic moment vector per unit volume*. When the system of interest involves material that displays intrinsic magnetic moments, \mathcal{H} must be replaced

by \mathcal{B} , the *magnetic induction per unit volume*, that includes the additional magnetic effects. In this particular formulation, the thermodynamic coordinates remain unchanged; only the potential energy of the system is altered. This expression, analogous to the lifting of a given mass of material against a gravitational field, is normally not of interest.

As an alternative, we introduce a local current density, $\mathbf{J}(\mathbf{r})$, that is responsible for generating the magnetic field \mathcal{H} and that is associated with a steady vector potential $\mathcal{A}(\mathbf{r})$. The associated work element is specified by $dW = (1/c) \int_V d^3\mathbf{r} \mathbf{J} \cdot d\mathcal{A}$, where c is the velocity of light. We next introduce Maxwell's relation $\nabla \times \mathcal{H} = (4\pi/c)\mathbf{J}$, which applies when the electric displacement vector is independent of time and when \mathbf{J} is the free current density. Thereby, we set $dW = (4\pi)^{-1} \int d^3\mathbf{r} d\mathcal{A} \cdot (\nabla \times \mathcal{H})$. On using line (f) of Table 1.3.I, the work increment then reads $dW = (4\pi)^{-1} \int d^3\mathbf{r} [\mathcal{H} \cdot (\nabla \times d\mathcal{A}) - \nabla \cdot (\mathcal{H} \times d\mathcal{A})]$. The integration extends over the entire region where \mathcal{H} is present. The second integral, involving a divergence, is rewritten by application of Gauss' theorem, wherein $\mathcal{H} \times d\mathcal{A}$ is evaluated over an arbitrary surface that may be drawn infinitely far away. This portion of the integral may be discarded, leaving us with the first part that involves $\nabla \times d\mathcal{A} = d\mathcal{B}$, where \mathcal{B} was introduced earlier. We thus obtain

$$dW = (4\pi)^{-1} \int d^3\mathbf{r} \mathcal{H} \cdot d\mathcal{B}. \quad (1.5.7a)$$

This formulation presents problems because the integral extends over all space. Also, the independent variable is \mathcal{B} , which includes the response of the material to the externally applied magnetic field \mathcal{H} . Only the latter is subject to direct experimental control. For most practical applications it is more convenient to use the expression, derived in Section 1.6,

$$dW = \int_V d^3\mathbf{r} \mathcal{H}_0 \cdot d\mathcal{M}, \quad (1.5.7b)$$

where $\mathcal{M} = (4\pi)^{-1}(\mathcal{B} - \mathcal{H}_0)$ and \mathcal{H}_0 is the *applied magnetic field* prior to the introduction of the sample. The integration involves only the volume of the specimen, since \mathcal{M} vanishes outside its confines. We have not included the work required to set up the magnetic field in vacuum prior to insertion of the sample. Also, it is usually appropriate to introduce the linear relation $\mathcal{M} = \chi\mathcal{H}$, where χ is the *magnetic susceptibility*; alternatively, $\mathcal{M} = \chi_0\mathcal{H}_0$. One should note the sign difference in comparing Eqs. (1.5.6c) and (1.5.7b).

Two-Dimensional Films

Consider a thin film mounted on a wire frame (Figure 1.5.4) that is stretched by length dx through the application of a force f ; the work element is given by $dW = f dx$. The area increase is $dA = 2l dx$, where l is the length of the frame perpendicular to the applied force; the factor 2 arises because there is a film on both sides of the wire frame. Thus, $dW = (f/2l)dA$ conventionally one defines the *surface tension* by $\gamma \equiv f/2l$, whence

$$dW = \gamma dA. \quad (1.5.8)$$

The above relation also applies if one considers the work element for increasing the surface area of a body in the amount dA .

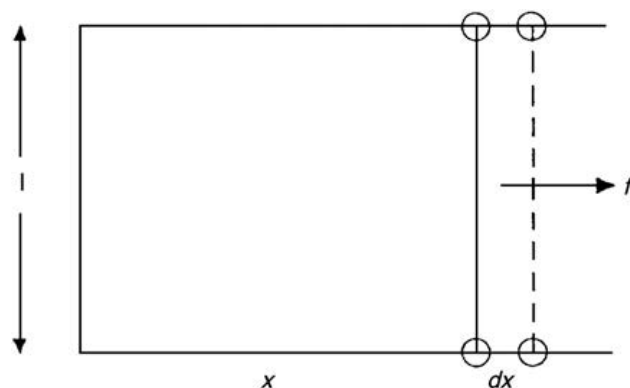


FIGURE 1.5.4

Setup for expanding a film stretched over a wire frame.

Chemical Work

For completeness, we cite in preliminary fashion the changes in a system that are brought about through transfer of chemical species i in amounts of dn_i moles, across the boundaries of an adiabatically insulated, isochoric system. As in all other cases, this action requires an agent (a force as defined in Section 1.4) to affect the process. This force constitutes the intensive variable, f_i , of Eq. (1.5.1), conjugate to dn_i , required to execute the chemical work. It is known as the *chemical potential* μ_i . In Chapter 2, we shall investigate its nature and properties in detail, and show that μ indeed represents a driving force for compositional changes. For now, we specify the element of work under the action of the chemical potential μ_i as

$$\delta W_i = \mu_i dn_i. \quad (1.5.9)$$

Because of its obvious relevance to chemical processes, this formulation is of special importance in chemical thermodynamics.

Elongation of Springs

We show by a simple example how to deal with a case where the intensive variables of the surroundings do not match those of the system.¹ Let a mass M be attached to a weightless spring, as shown in Figure 1.5.5. At equilibrium, the spring is extended to its normal length x_0 and the mass point is stationary. In this figure, an applied force F is shown as pointing to the right; it elastically extends the

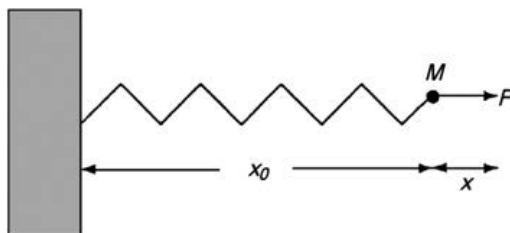


FIGURE 1.5.5

Schematic diagram depicting a massless spring with an attached mass point.

spring to length $x > x_0$. By Hooke's law, the applied force is $F = k(x - x_0)$, where k represents the force constant of the spring. Under contraction, F points in the opposite direction, so that $x < x_0$. Let the force $F = F_s$ first be applied quasi-statically, so that it barely exceeds the internal force of the spring at each stage of the process; then the velocity v of the mass point during the extension process is essentially zero. The work carried out on the system in this action is given by

$$W = \int_{x_0}^{x_1} F_s dx = \int_{x_0}^{x_1} k(x - x_0) dx, \quad (1.5.10a)$$

where x_1 is the extension of the spring at the conclusion of the process. Integration leads to

$$W = k(x_1 - x_0)^2 / 2 \quad (1.5.10b)$$

if k is independent of x . In the absence of other work and under adiabatic conditions, the increase in the function of state is stored as potential energy within the spring.

Now apply a force F in excess of the force F_s needed to extend the spring quasi-statically. Then Eq. (1.5.10a) may be rewritten identically as

$$W = \int_{x_0}^{x_1} F_s dx + \int_{x_0}^{x_1} (F - F_s) dx, \quad (1.5.11a)$$

where the first term is treated as before. The second contribution describes an acceleration of the mass point m arising from the excess applied force. The initial velocity of the mass point is $v = v_0 = 0$, which reaches v_1 when the spring is extended to length x_1 . By Newton's first law, $F - F_s = m d^2x/dt^2$; with $v = dx/dt$, $(d^2x/dt^2)dx = (dv/dt)v dt = v dv$. Hence, the second term in Eq. (1.5.11a) becomes $\frac{1}{2}m(v_1^2 - 0)$, and Eq. (1.5.10a) is altered to read

$$W = \frac{1}{2}k[x_1 - x_0]^2 + \frac{1}{2}m v_1^2, \quad (1.5.11b)$$

where the energy change of the system now involves not just the potential energy contribution but a kinetic energy term as well. This example clearly emphasizes that only in the case of quasi-static processes, one may replace the applied external force by the opposing internal force of the system.

SUMMARY

In closing, we note that in all the above cases (as well as in situations that have not been taken up here), the element of work is specified by the (dot) product of an intensive variable with the differential of an extensive variable. Where more than one force is operational, one must sum over the various elements of work. This important conclusion is summarized by the mathematical formulation,

$$dW = \sum_i \mathbf{Z}_i \cdot d\mathbf{z}_i, \quad (1.5.12a)$$

in which the \mathbf{Z}_i represent the appropriate generalized forces, and the \mathbf{z}_i represent the corresponding conjugate displacements. Once again, the integration of Eq. (1.5.12a) must be taken along a particular path; in general, no unique result is found even for fixed initial and final states.

Path-Independent Line Integrals

We have almost endlessly repeated that work, as expressed by

$$W_i = \int_{x_1}^{x_2} \mathbf{f}_i \cdot d\mathbf{x} \quad (1.5.12b)$$

ordinarily depends on path taken, i.e., on the manner in which the force varies with displacement, when \mathbf{x} is changed from \mathbf{x}_1 to \mathbf{x}_2 . For obvious reasons, it is difficult to develop a sensible theory if, for a specific difference in end points, the integrals (changes in properties) depend on the chosen path. One is thus led to the important task of seeking out integrals that depend solely on the end points—quantities that were described in Section 1.3 as *functions of state*. Such integrals also vanish identically when $\mathbf{x}_1 = \mathbf{x}_2$.

For this purpose, consider a process for which we select a particular coordinate $x_1 = 0$ that is arbitrary but, once chosen, invariant. We may then introduce a function $\Phi(\mathbf{x}_2)$ defined by

$$\Phi(\mathbf{x}_2) = - \int_0^{\mathbf{x}_2} \mathbf{f}(\mathbf{x}) \cdot d\mathbf{x}, \quad (1.5.13)$$

called a *potential function* which depends solely on the quantity \mathbf{x}_2 ; the minus sign has been introduced as part of the convention. The difference between the potential function at \mathbf{x}_1 and \mathbf{x}_2 is given by

$$\Phi(\mathbf{x}_2) - \Phi(\mathbf{x}_1) = - \int_{\mathbf{x}_1}^{\mathbf{x}_2} \mathbf{f}(\mathbf{x}) \cdot d\mathbf{x} = \int_{\mathbf{x}_1}^{\mathbf{x}_2} [\nabla \Phi(\mathbf{x})] \cdot d\mathbf{x}. \quad (1.5.14)$$

The right hand is obtained through line (j) of Table 1.3.I; it involves the definition of the divergence symbol. Note that now the central integral is replaced by one that involving a gradient, and so it truly depends only on the choice of end points; when Eq. (1.5.13) obtains, we encounter a function of state. Moreover, since the integrands must match, we find that

$$\mathbf{f} = -\nabla \Phi(\mathbf{x}). \quad (1.5.15)$$

That is to say, when a function with the properties Φ can be found, the vector \mathbf{f} as well as its three spatial components are determined by the negative gradient of this single scalar potential function. It is then simplest to determine the potential function first and then take its gradient to find the components of the force vector. This extraordinary property invites further exploration that illuminates the properties of functions of state.

For this purpose, we examine *Stokes' theorem*, line (l) of Table 1.3.I, in the form

$$\oint \mathbf{F} \cdot d\mathbf{x} = \oint (\nabla \times \mathbf{F}) \cdot d^2\mathbf{x}, \quad (1.5.16)$$

where the left-hand side involves any closed boundary path that is located on a surface region and the integral on the right is taken over a surface that bounds the region of interest. Any function of state \mathbf{F} taken around a closed loop must vanish; then, the integrand on the right vanishes as well, so that

$$\nabla \times \mathbf{F} = 0. \quad (1.5.17)$$

In this situation, the three components of the function of state F are not independent; when Eq. (1.5.17) is expanded as shown in Eqs. (1.3.24 and 1.3.25), one obtains

$$\partial F_x / \partial y = \partial F_y / \partial x, \quad \partial F_z / \partial y = \partial F_y / \partial z, \quad \partial F_z / \partial x = \partial F_x / \partial z, \quad (1.5.18)$$

which exhibits stringent requirements to which the function F is subject.

On finally setting $F = -\nabla\Phi$ and then taking $F_x = -\partial\Phi/\partial x$, $F_y = -\partial\Phi/\partial y$, and $F_z = -\partial\Phi/\partial z$, and along with Eq. (1.5.18), one finds that $(\partial^2\Phi/\partial x\partial y - \partial^2\Phi/\partial y\partial x) = 0$, and similarly for the other components. Thus, the second-order cross-derivatives of the potential function taken in either order are the same—a comforting result.

The potential function in Eq. (1.5.13) is a mathematical construct reminiscent of the potential energy commonly introduced in elementary treatments. However, the two ideas should not be confused; the potential energy associated with the concept of energy is taken up below. By contrast, the potential Φ is invoked in conjunction with line integrals that are independent of the path, i.e., that vanish when taken around a loop.

Comment and Queries

- 1.5.1. This material is taken from a lecture by Professor J.W. Richardson of Purdue University.
- 1.5.2. It is stated that the element of work always involves an intensive and the differential of an extensive variable. Yet, in Eqs. (1.5.6) and (1.5.7), only intensive quantities seem to be present. How is this apparent contradiction resolved?
- 1.5.3. What changes in the analysis of the spring performance must be introduced when the spring itself has a nonzero mass?

1.6 The Element of Work for a System Subjected to Electromagnetic Fields

We here introduce a detour that may be skipped on first reading. It provides a derivation leading to Eqs. (1.5.6c) and (1.5.7b), beginning with the Maxwell equations

$$\nabla \times \mathcal{E} + (1/c)\partial\mathcal{B}/\partial t = 0 \quad (1.6.1a)$$

$$\nabla \times \mathcal{H} - (1/c)\partial\mathcal{D}/\partial t = 4\pi\mathbf{J}_f/c. \quad (1.6.1b)$$

Here E , \mathcal{D} , \mathcal{H} , \mathcal{B} and \mathbf{J}_f represent, respectively, the electric field, electric displacement, magnetic field, magnetic induction, and free current density (i.e., the current densities that can be controlled experimentally); c is the speed of light. Form the scalar product of Eq. (1.6.1a) with \mathcal{H} and of Eq. (1.6.1b) with \mathcal{E} and subtract, to obtain

$$\mathcal{H} \cdot (\nabla \times \mathcal{E}) - \mathcal{E} \cdot (\nabla \times \mathcal{H}) + (1/c)\mathcal{H} \cdot (\partial\mathcal{B}/\partial t) + (1/c)(\mathcal{E} \cdot \partial\mathcal{D}/\partial t) = -(4\pi/c)\mathcal{E} \cdot \mathbf{J}_f. \quad (1.6.2)$$

Next, introduce the vector identity $\mathcal{H} \cdot (\nabla \times \mathcal{E}) - \mathcal{E} \cdot (\nabla \times \mathcal{H}) = \nabla \cdot (\mathcal{E} \times \mathcal{H})$, line (f) (Table 1.3.I), to obtain

$$\nabla \cdot (\mathcal{E} \times \mathcal{H}) + (4\pi/c)\mathcal{E} \cdot \mathbf{J}_f + (1/c)\mathcal{H} \cdot (\partial\mathcal{B}/\partial t) + (1/c)(\mathcal{E} \cdot \partial\mathcal{D}/\partial t) = 0. \quad (1.6.3)$$

Now integrate over all space. By Gauss' theorem, $\int d^3\mathbf{r} \nabla \cdot (\mathcal{E} \times \mathcal{H})$ may be transformed into a surface integral enveloping all the fields. In order to encompass all charges, the surface integration must be extended to infinitely remote boundaries where the fields definitely vanish. This term therefore drops out, leaving

$$\int d^3\mathbf{r} \mathcal{E} \cdot \mathbf{J}_f dt = (1/4\pi) \int d^3\mathbf{r} (\mathcal{E} \cdot d\mathcal{D} + \mathcal{H} \cdot d\mathcal{B}). \quad (1.6.4)$$

We rewrite the left-hand integrand in the form

$$\mathcal{E} \cdot \mathbf{J}_f = \mathcal{E} \cdot \rho_f \mathbf{v}_f = [\rho_f \mathcal{E} + c^{-1} \rho_f \mathbf{v}_f \times \mathcal{B}] \cdot \mathbf{v}_f \equiv \mathbf{f}_f \cdot \mathbf{v}_f, \quad (1.6.5)$$

in which ρ_f and \mathbf{v}_f are the free charge carrier density and carrier velocity, respectively. On the right, we took note of line (a) (Table 1.3.I) by inserting the vector identity $\mathbf{v}_f \cdot (\mathbf{v}_f \times \mathcal{B}) = \mathcal{B} \cdot (\mathbf{v}_f \times \mathbf{v}_f) \equiv 0$, which holds because the cross-product $\mathbf{v}_f \times \mathbf{v}_f$ vanishes identically. This corresponds to the fact that a charged particle moving in a magnetic field does no work. The quantity in square brackets represents the *Lorentz force density*, designated by \mathbf{f}_f . With Eq. (1.6.4) in mind, we finally obtain

$$\mathfrak{d}W = - \int d^3\mathbf{r} \mathcal{E} \cdot \mathbf{J}_f dt = - \int d^3\mathbf{r} \mathbf{f}_f \cdot \mathbf{v}_f dt = (1/4\pi) \int d^3\mathbf{r} (\mathcal{E} \cdot d\mathcal{D} + \mathcal{H} \cdot d\mathcal{B}). \quad (1.6.6)$$

as the increment of work.¹ This represents an alternate derivation of Eqs. (1.5.6a) and (1.5.7a).

We now follow Heine (1956) in taking note of the mathematical identity

$$\begin{aligned} \mathcal{E} \cdot d\mathcal{D} + \mathcal{H} \cdot d\mathcal{B} &\equiv \mathcal{E}_0 \cdot d\mathcal{D}_0 + \mathcal{H}_0 \cdot d\mathcal{B}_0 + (\mathcal{E} \cdot d\mathcal{D}_0 - \mathcal{D} \cdot d\mathcal{E}_0) + (\mathcal{H}_0 \cdot d\mathcal{B} - \mathcal{B}_0 \cdot d\mathcal{H}) \\ &+ (\mathcal{D}_0 \cdot d\mathcal{E}_0 - \mathcal{E}_0 \cdot d\mathcal{D}_0) + (\mathcal{B}_0 \cdot d\mathcal{H}_0 - \mathcal{H}_0 \cdot d\mathcal{B}_0) + \mathcal{E} \cdot (d\mathcal{D} - d\mathcal{D}_0) + (\mathcal{D} - \mathcal{D}_0) \cdot d\mathcal{E}_0 \\ &+ \mathcal{B}_0 \cdot (d\mathcal{H} - d\mathcal{H}_0) + (\mathcal{H} - \mathcal{H}_0) \cdot d\mathcal{B}. \end{aligned} \quad (1.6.7)$$

The subscripted vectors represent field variables arising from fixed charge and current distributions existing prior to insertion of the sample, and the remaining vectors represent corresponding quantities when the sample is present in the field.

We now integrate over all space. In the first two terms, we consider properties of the electromagnetic field in the absence of the sample. Then $\mathcal{B}_0 = \mathcal{H}_0$ and $\mathcal{D}_0 = \mathcal{E}_0$. The third term may be rewritten as $(\mathcal{E} - \mathcal{D}) \cdot d\mathcal{E}_0 = -4\pi \mathcal{P} \cdot d\mathcal{E}_0$; here, the integration may be restricted to the volume of the sample, since \mathcal{P} vanishes elsewhere. The fourth term similarly reads $\mathcal{H}_0 \cdot (d\mathcal{B} - d\mathcal{H}) = 4\pi (\mathcal{H}_0 \cdot d\mathcal{M})$; again, the integration may be restricted to the sample volume since elsewhere $\mathcal{M} \equiv 0$. The fifth and sixth sets vanish automatically. When the integration is carried out, each of the last four terms vanishes as well, on account of a vector theorem derived by Stratton² to which the reader is referred for further details. This leaves

$$\mathfrak{d}W = (1/4\pi) \int d^3\mathbf{r} (\mathcal{E}_0 \cdot d\mathcal{E}_0 + \mathcal{H}_0 \cdot d\mathcal{H}_0) - \int_V d^3\mathbf{r} \mathcal{P} \cdot d\mathcal{E}_0 + \int_V d^3\mathbf{r} \mathcal{H}_0 \cdot d\mathcal{M}. \quad (1.6.8)$$

In the above, the first two integrals extend over all space; they specify the work increment required to set up the electromagnetic field in free space. These quantities normally are only of secondary interest. The remainder relate to the additional work involved in immersing the sample into the preexisting field that is held fixed. One should note the difference in sign between the third and fourth terms, and the nonsymmetric disposition of the field and response variables in these two integrals. In particular, it is the magnetization that

appears as the control variable in the magnetic contribution, whereas it is the electric field that serves this purpose in the electric polarization. More will be said about this asymmetry in Section 5.8.

Remark and Reference

- 1.6.1.** The sign convention requires a comment. Positive current proceeds in the direction of the electric field; hence, the dot product of the integrand is positive. On the other hand, the charges, flowing from a region of higher to lower potential, have lost energy, which is transferred (as work under isothermal conditions) to the surroundings. This process thus necessitates the minus sign in specifying the work performance. If the carriers are negatively charged, then the sign of ρ_f and that of \mathbf{v}_f are both reversed, so that the conclusion is still the same.
- 1.6.2.** J.A. Stratton, *Electromagnetic Theory* (McGraw-Hill, New York, 1941), p.111.

1.7 The First Law of Thermodynamics

At last, back to thermodynamics! We start by setting up our first thermodynamic function of state. For this purpose, we invoke an experience of mankind: work W_a performed *under adiabatic conditions*, in taking a given system from an initial state with coordinates $\{\mathbf{x}_i\} = (x_1, x_2, \dots, x_n)_i$ to a final state with coordinates $\{\mathbf{x}_f\} = (x_1, x_2, \dots, x_n)_f$, is independent of the type of work executed and is independent of the path taken in proceeding from $\{\mathbf{x}_i\}$ to $\{\mathbf{x}_f\}$. We therefore associate with this change of state a mathematical function of state, which is called the (*internal*) *energy* E , whose difference, $\Delta E = E\{\mathbf{x}_f\} - E\{\mathbf{x}_i\} = W_a$ uniquely corresponds to work of *any type* that is performed *under any adiabatic conditions* in bringing the system from any specific initial state $\{\mathbf{x}_i\}$ to any specific final state $\{\mathbf{x}_f\}$.

If the same process is now executed under nonadiabatic conditions, the above assertion no longer obtains, which would seem severely to limit the usefulness of the above concept. However, processes that differ from those prevailing under adiabatic conditions must now be taken into account; these will be dealt with shortly. This fact permits us to broaden the original claim. It is thus asserted that, more generally, any particular change in the state of a system can always be correlated with a unique change in energy. We shall later learn how to determine such an energy change by experiment or by theory.

This experience of mankind is formalized in a statement of the *first law of thermodynamics*:

Any process whatsoever may be correlated with a function of state, called the internal energy, E , whose change depends solely on the initial and final thermodynamic coordinates of the system.

In other words, for any given transformation of the system from state $\{\mathbf{x}_i\}$ to $\{\mathbf{x}_f\}$, there exists a unique energy difference $\Delta E = E_f - E_i$ that characterizes this change, no matter how it is accomplished. In particular, it does not matter whether the process is carried out reversibly or irreversibly. Obviously, this assertion is not useful until one knows how to determine the energy difference for all conceivable processes. The manifold ramifications of this idea will be gradually developed as we go along. Meanwhile, note that the discussion relates to *changes* of energy; the first law has nothing to say about the value of E itself. As will also be evident below, in connection with the differential formulation, E can

only be specified to within an arbitrary constant that generally is of no particular interest: in any process, this quantity appears both in the initial and in the final state and thus cancels out.

The above law leads to important consequences. While, as claimed earlier, in an adiabatic process, $\Delta E - W_a = 0$, whereas in any nonadiabatic process, the work performed, W , differs from W_a , so that $\Delta E - W \neq 0$. Inequalities are not particularly pleasant quantities to deal with. We can rectify this situation by introducing a *deficit function* Q , called the *heat transfer*, that permits us to restore the equality. Q is so constructed that $Q - [\Delta E - W] = 0$. This rather austere definition provides very little insight on the physical nature of “heat,” nor on methods for its detection; more on that later on. For the moment, suffice it to state that heat transfers attend to all changes in properties of a system that are not accomplished by execution of work as defined in Section 1.5, or by compositional changes described in Section 1.12. As experienced by humans, heating effects normally manifest themselves as increases in the temperature of the system (hotness levels, in conventional language) or as changes in the phase structure of the system.

In any given operation, ΔE may be determined through performance of work under adiabatic conditions; W is then either measured or calculated for the same change when executed under the actual (nonadiabatic) operation. Then Q is found as the difference between these two determinations. If no adiabatic path exists for proceeding from state i to state f , one can generally find an intermediate state l such that by performance of work W'_a and W''_a , one can execute the adiabatic transformations $i \rightarrow l$ and $l \rightarrow f$, respectively. Let ΔE_{il} , ΔE_{lf} and ΔE_{if} be the corresponding energy changes; then, since energy is a function of state $\Delta E_{if} = \Delta E_{il} + \Delta E_{lf} = W'_a + W''_a$, the desired energy change can be determined via separate measurements of W'_a and W''_a .

Here is an important point: implicit in the above is the idea that energy changes can be brought about *solely* through interactions of the system with its surroundings via the performance of work or transfer of heat. *Purely internal reconfigurations of thermodynamic coordinates do not alter the energy of the system.*¹

We now write the first law in the following mathematical form:

$$\Delta E = Q + W. \quad (1.7.1)$$

As noted earlier, Q and W represent the two different manifestations of *energy in transit* across the boundaries of the system; these incur *changes* in the energy of the system but do not represent energies per se. According to Eq. (1.7.1), the energy of the system is increased by rendering $Q > 0$ and $W > 0$. Thus, in the present convention,² for $Q > 0$, heat is said to flow *into* the system, and for $W > 0$, work is said to be performed *on* the system. Conversely, the energy is diminished by having $Q < 0$ and $W < 0$, in which case heat is said to flow *out of* the system into its surroundings, and work is said to be done *by* the system on its surroundings.² For all adiabatic processes, $Q = 0$.

We next present the first law in differential form of Eq. (1.7.1) as

$$dE = \mathfrak{d}Q + \mathfrak{d}W. \quad (1.7.2)$$

Here, again a distinction is made between d as a differential symbol for a function of state, while \mathfrak{d} is reserved as a differential symbol for path-dependent quantities that change with alterations of the chosen path. As defined above, energy qualifies as a function of state. We also broaden the concept of adiabatic processes; in any such operations, $\mathfrak{d}Q = 0$ at every infinitesimal stage of the process. Also, using the subscripts i and r to signify irreversible and reversible operations, we may set

$$dE = \mathfrak{d}Q_r + \mathfrak{d}W_r = \mathfrak{d}Q_i + \mathfrak{d}W_i \quad (1.7.3)$$

as a direct consequence of E being a function of state. Furthermore, the energy differential involving the thermodynamic coordinates x_1, x_2, \dots, x_n must be expressible in analytic form (Section 1.3) as

$$dE = \sum_{j=1}^n (\partial E / \partial x_j) dx_j. \quad (1.7.4)$$

A similar *unique* expression for Q and W is clearly inappropriate.

Finally, the statement $Q = W = 0$ directly leads to the *law of conservation of energy* as a corollary to the first law. Contrary to intuition, in an isolated system, the energy is constant, no matter what processes occur totally within its borders. This then disposes of perpetual motion machines.

Energy as a Function of State

As an introduction to later developments, we note that in a reversible process, the element of work $-P(V)dV$ requires that the energy be minimally dependent on volume: $E = E(V)$, the functional form to be specified later. Similarly, according to Eq. (1.5.9), in a reversible transfer of chemical species to or from a system, the differential change in energy is given by $dE = \mu_i dn_i$, which requires that E must also feature the various n_i as independent variables: $E = E(n_1, n_2, \dots, n_r)$.

Consider now a *reversible* adiabatic process across the boundaries of a system. Since in the present case energy is an analytic function of V and of the n_i , we may use Eq. (1.7.4) to write (the subscript S here denotes an adiabatic process)

$$dE_S = \left(\frac{\partial E}{\partial V} \right)_{S, n_i} dV + \sum_i \left(\frac{\partial E}{\partial n_i} \right)_{S, V, n_{j \neq i}} dn_i. \quad (1.7.5)$$

A comparison with the expression for the elements of work, relations (1.5.3) and (1.5.9), along with Eq. (1.7.3), shows that the pressure and chemical potential are specified by

$$P = - \left(\frac{\partial E}{\partial V} \right)_{S, n_i} \quad \text{and} \quad \mu_i = \left(\frac{\partial E}{\partial n_i} \right)_{S, V, n_{j \neq i}}. \quad (1.7.6)$$

The first relation may serve as one technique to determine E (for adiabatic processes) via integration of an equation of state of the general form $P = P(V, n_i)_{S, n_i}$. The second expression is of use only after ways are found to express the partial derivative in terms of measurable quantities. We later show how to determine μ_i either experimentally or via the equation of state, and learn why this quantity is called a *chemical potential*.³

Further Remarks on the Concept of Heat

So far, heat has been introduced as a rather aethereal quantity, without any attempts to indicate what heat really *is*; neither has it been shown in what way this concept differs from that of work. This distinction is not a trivial matter, as is illustrated by a simple example: consider a block of material surrounded by heater wires. If the boundaries of the system are drawn so as to exclude the heating unit, then any warming of the block by circulation of current through the external wires is generally considered to be a heating process. If the boundary includes the heater wire, the warming of the system

is usually attributed to the work required to circulate the current. Clearly, it is problematic to have a definition depending on how one draws a boundary between a given system and its surroundings.

Any attempt to be tidy in making a distinction between heat and work engenders conceptual problems. It may nevertheless be helpful to examine different cases that illustrate how work execution differs from heat transfer. A case will now be made for distinguishing between (a) any change in energy of a system that cannot take place *except* by the execution of processes of the type $\int Z_i dz_i$ along a particular path, such as identified in Section 1.5, and (b) a change in energy that is brought about by processes differing from those discussed in Section 1.5. The former is considered to involve the *performance of work*, while the latter is classified as a *transfer of heat*.

Some examples may clarify the abovementioned distinction: clearly, any change in volume of a system due solely to actions of external forces directed on the boundaries of the system is to be classified as work. Less intuitive is a variant of the Joule experiment, in which a paddle wheel, imbedded in a liquid at constant volume and composition, is made to stir the liquid by a descending weight in the Earth's gravitational field. Although the same resulting rise in temperature could be achieved by conventional heating, and though (with proper precautions) no macroscopic coordinates other than temperature are changed, the paddle wheel process requires equivalent work performance through action of an outside source that may well be far removed from the system. While directly connected to the system the paddle wheel is not a part of the system. Nothing happens unless the weight is allowed to descend; the energy increase of the system is governed by the extent of the descent. The crucial point is that the initiation of the process by the outside agent and the resulting changes in the system are directly connected. This process therefore falls into the category of work, as in (a) previously. Contrast this with the placement of the system in the radiation field of the Sun: just about everyone would agree that this process is a heat transfer. Usually, one does not inquire about the nuclear processes in the Sun that generate the sunshine; these operate quite independently of what goes on inside the system when exposed to the sunshine. This type of indirect interaction is associated with heat transfer.

Similarly, if heater wires are imbedded in a body, nothing happens until current is made to flow through the wires by discharge of a current source, such as a battery; the discharge process in the battery initiates a rise in temperature of the body. The surroundings (the heater wires) are in intimate, direct contact with the system, but the wires are not part of the system. Again, the end result is a direct consequence of work performance and takes place exactly in step with the battery operation. However, if the heater wires are placed outside the body, the temperature rise depends on energy transfer from the separated heater wires to the cooler body across its boundaries. In that case the battery discharge can no longer be directly linked to the temperature rise of the system; we deal with heat transfer processes. Actually it does not matter what agency is used to warm up the wires: whether its distant ends are heated by a candle, or results from concomitant changes of the battery, is immaterial. In such cases the agents of change in surroundings are not directly linked to those within the system; they usually are not taken into account.

The exposure of a body to the rays of the Sun clearly represents an instance of heat transfer, as is microwave irradiation, or X-ray exposure. As stated previously, the source of the energy supply is left out of account; there is no direct contact between the system and its separated source of energy. By way of contrast, as indicated in Section 1.5, the placement of a body in a gravitational field, or similar actions on a charged or magnetized body in an electromagnetic field, or their movements within such fields, represent instances of work performance; the body is placed directly within the field with which it interacts. Again, we are not generally concerned about how these fields were generated in the first place.

Another case of interest is the rise in temperature of a block that is dragged over a rough surface against a frictional force. Here part of the effort is dissipated as a change of the surroundings; the remainder leads to

a rise in temperature of the system. In principle, as we show later, the extent to which the energy of the system is thereby increased may be determined via heat capacity measurements that monitor the temperature rise, which depends in part in how fast and for how long the pulling effort is sustained. Again, the fact that the same temperature change in the system could have been brought about by direct heating is immaterial; the change in state through frictional means requires the execution of work.

By way of summary and amplification, work performance is defined here as a process requiring a direct interaction between a system and its surroundings that may be rendered equivalent to, directly or indirectly, the movement of a weight in the earth's gravitational field. In most but by no means all cases, such processes are accompanied by changes in the macroscopic variables that characterize the state of the system and of the actuating surroundings. By contrast, heat transfer is defined in terms of processes in which the energy of a system is changed by indirect interactions with surroundings that operate independently of what goes on inside the system. Stated differently, any process that cannot be directly described by, or otherwise associated with, generally path-dependent integrals $\int Z_i dz_i$ is classified as a heat transfer. However, this attempted tidiness is always compromised by secondary processes that inevitably take place. For example, the heating process is always accompanied by thermal expansion of a system, which does not involve the action of an external force. One must thus distinguish between volume changes so incurred, as opposed to those generated by the action of external forces—symptomatic again of the difficulties of achieving clean classifications.

Finally, it should be clear that the above classification is to be taken as a *definition* for use in later developments. What matters for present purposes is the analysis by which a correct accounting of the energy changes in a system due to all relevant processes may be achieved, regardless of how they are classified. However, this disclaimer is no longer appropriate when it comes to the discussion of the second law.

We shall have more to say about heat after we introduce the second law.

The First Law of Thermodynamics as a Parable

Callen¹ has provided an interpretation of the first law of thermodynamics in terms of a parable that bears repeating. A certain person owns a rectangular swimming pool; he allows water to enter or leave through an inlet and outlet and daily compares the height of the water level with the amount of water that has flowed through the water meters attached to the inlet and outlet.

In general, the owner notes no detailed correlation between the water meter readings and the change in water level in the pool, but he notes that on rainy days, the pool contains more than the expected amount, and on very dry days, less water is present than anticipated. So the owner is led to cover the pool with a tarpaulin. At that point, the owner finds that indeed the change in water level can be balanced precisely with the rates of water passage through the inlet and outlet.

The analogy with the energy of a system should be clear. The covered pool is the analog of an adiabatic system; changes in water levels correspond to energy changes. Water flowing through the inlet and outlet corresponds to positive and negative work, respectively. When the tarpaulin is removed, the water added through rainfall or diminished by evaporation corresponds to heat influx and outflow. In these circumstances, the book-keeping requires that water gained through rainfall or lost through evaporation be taken into consideration when tracking changes in water level.

Notice finally that the liquid in the pool is just water; one cannot differentiate between liquid that entered or left through the faucets, as compared to water that was accumulated or lost through rainfall or evaporation. This should render more understandable earlier statements that heat and work transfers

represent energy in transit across boundaries, and that they cannot be identified as pieces of energy within the system.

All parables, being analogies, are to some extent misleading. Chief among the problems is the fact that, unlike water, heat is not a conserved quantity. However, this should not deter you from pondering the lessons of this very nice tale.

Reference

1.7.1. H.B. Callen, *Thermodynamics* (Wiley, New York, 1960).

Notes

- 1.7.1. This idea is quite counterintuitive. Take as an example an explosive recombination of hydrogen and oxygen *that is not communicated to the outside world*; it is difficult to swallow the fact that there has been no energy change in the system. The point is that the first law does not assert that “nothing has happened”; in fact, the concomitant changes in state are addressed by the second law, and its consequences are spelled out in Section 2.10. Rather, the thermodynamic coordinates of the system have been reconfigured in such a way that the potential energy of the two gases in the chamber at the original temperature has been converted into an appropriate amount of kinetic energy of remaining gases and in the generation of water at a higher temperature. As long as the system remains isolated during the entire process, there has been no change in its energy. The same change may be brought about quasi-reversibly by letting the system sit there, allowing the gases in the isolated system to interact nonexplosively over many eons. That such an operation can be effected without any energy change is not so counterintuitive.
- 1.7.2. This practice is not universally adhered to. Particularly in older treatments of the subject, work performed on and by the system was characterized by $W < 0$ and $W > 0$, respectively. This was compensated for by writing the first law in the form $\Delta E = Q - W$. You should always check which convention is being followed.
- 1.7.3. One should note that the flow of matter in response to a concentration gradient is in fact associated with a difference in chemical potential, as will be shown later. The infinitesimal transfer of matter $\mu_i dn_i$ is analogous to the volume change actuated by the use of pressure, $-PdV$, which makes it plausible that $\mu_i dn_i$ should be classified as “chemical work”.
- 1.7.4. For a classification that invokes internal degrees of freedom of the system, see T.L. Hill, *An Introduction to Statistical Thermodynamics* (Dover, New York, 1986), Chapter 1. Brief mention of this concept is also included in Chapter 10.
- 1.7.5. State whether irradiation of a sample in a nuclear reactor can be indirectly linked to the falling of a weight in the earth’s gravitational field; and whether the process should be classified as work or as heat.

1.8 The Second Law of Thermodynamics

We now closely examine another fundamental law that underlies our further development.

The second law of thermodynamics has been stated in many different equivalent ways. One approach, which seems pedagogically attractive, involves a formulation rather similar to that of the first law, where we had linked work performance under adiabatic conditions to energy as a function of state. In a similar manner, we now link the path-dependent transfer of heat *under reversible conditions* to another function of state, termed the *empirical entropy*, symbolized by s (or, later, the *metrical entropy*, S). The relation is not as simple as was the case for the first law, but the methodology is the same. In short, it is claimed as part of the *second law of thermodynamics* that

A reversible incremental transfer of heat, $\delta_r Q$, between a given system and its surroundings is related to a new incremental analytic function of state, termed the empirical entropy, ds , through an integrating denominator, λ , whose physical significance is to be established.

In consequence, the second law may be formulated mathematically as

$$\delta_r Q / \lambda = ds. \quad (1.8.1)$$

The above, relatively simplistic, formulation may be supplemented by a more formal and sophisticated approach that comes under the heading of *Carathéodory's theorem*. This provides a solid mathematical grounding for providing conditions under which the Pfaffian form $\delta_r Q = \sum_i X_i dx_i$ may be converted via Eq. (1.8.1) into the exact differential for the function of state ds . However, the physical results of interest to experimentalists tend to be hidden behind a thicket of relatively sophisticated mathematical manipulations. For that reason, the Carathéodory's theory has been relegated to Chapter 9. You are urged to consult that exposition for a more rigorous approach to the subject. Meanwhile, let us examine the consequences of adopting Eq. (1.8.1). In the present context, the second law statement amounts to an affirmation that the requirements of Carathéodory's theory are met only by a study of reversible processes. Entropy changes linked to irreversible processes, i.e., to changes not under direct experimental control, will be discussed later.

The identification of λ involves a sequence of detailed steps in a very compelling logical presentation of abstract reasoning that is well within the grasp of undergraduates; we follow the line of reasoning of Buchdahl.¹ It hinges on the fact, set forth in Section 1.3, that an analytic function $F(x_1, x_2, \dots, x_n)$ has as its counterpart the differential form $dF = \sum_i (\partial F / \partial x_i) dx_i$. Every independent variable x_i in the function F is linked to a corresponding differential dx_i in the function dF .

We examine the physical significance of the *integrating denominator*, λ , so called because it changes a path-dependent quantity into a function of state. We do this again through the process of combining two different systems A and B into a composite unit C. In an infinitesimal process, designate the reversibly transferred heat between surroundings and system by $\delta_r Q_a$ and $\delta_r Q_b$ for the component parts, and by $\delta_r Q_c$ as the total for the internally equilibrated compound system; thus, $\delta_r Q_a + \delta_r Q_b = \delta_r Q_c$. On adopting Eq. (1.8.1), we then write

$$ds_c = (\lambda_a / \lambda_c) ds_a + (\lambda_b / \lambda_c) ds_b. \quad (1.8.2)$$

To determine the quantities λ , let the deformation coordinates of A and B be given by x_1, x_2, \dots, x_{n-1} ; t and y_1, y_2, \dots, y_{m-1} ; t respectively, where t is the *common* empirical temperature of the compound system. Then, according to the second law, via the execution of reversible heat transfer, we must be

able to generate an equation for the empirical entropy s_a as a function of state for subsystem a in terms of its independent variables: $s_a = s_a(x_1, x_2, \dots, x_{n-1}; t)$. This equation may be inverted by solving for, say, x_{n-1} in terms of $x_1, x_2, \dots, x_{n-2}, t, s_a$. In a similar manner for subsystem b , we solve for y_{m-1} in terms of $y_1, y_2, \dots, y_{m-2}; t; s_b$. We now assert the following:

- [1] s_c must be independent of $x_1, x_2, \dots, x_{n-2}; y_1, y_2, \dots, y_{m-2}; t$. If this were not so, Eq. (1.8.2) would necessarily contain additional terms involving $dx_1, dx_2, \dots, dx_{n-2}$, and $dy_1, \dots, dy_{m-2}, dt$, as explained below in Eq. (1.8.1).
- [2] The ratios λ_a/λ_c and λ_b/λ_c cannot depend on the variables cited in [1]; otherwise s_c would also depend on them, in contradiction to [1].
- [3] λ_c cannot depend on y_1, y_2, \dots, y_{m-2} ; otherwise, λ_a in Eq. (1.8.2) would have to depend on these same coordinates and in such a manner as to cancel out from λ_a/λ_c , for consistency with assertions [2] and [1]. However, λ_a cannot possibly be allowed to depend on the y coordinates of system B . By similar reasoning involving λ_b , the function λ_c must be independent of x_1, x_2, \dots, x_{n-2} .
- [4] Furthermore, λ_a cannot depend on x_1, x_2, \dots, x_{n-2} , and λ_b cannot depend on y_1, y_2, \dots, y_{m-2} . For, according to [3], these variables are missing from λ_c , whence the ratios λ_a/λ_c and λ_b/λ_c must also be free of these variables, to remain consistent with [1–3]. However, this argument does not apply to t , which is common to A , B , and C .
- [5] As a consequence of [1–4], the functions λ_a , λ_b , and λ_c can depend at most on the variables (s_a, t) , (s_b, t) , and (s_a, s_b, t) , respectively.
- [6] The functional dependences cited in [5] must have the form $\lambda_a = \varphi_a(s_a)T(t)$, $\lambda_b = \varphi_b(s_b)T(t)$, $\lambda_c = \varphi_c(s_a, s_b)T(t)$, in which $T(t)$ is a *common, though completely arbitrary* function of the empirical temperature t ; for, this function cancels from the ratios λ_a/λ_c and λ_b/λ_c in Eq. (1.8.2), so as to remain in agreement with [2].
- [7] In summary, we are left with the fundamental relations

$$\begin{aligned} \delta_r Q_a &= T(t)\varphi(s_a)ds_a \equiv T(t)dS_a; & \delta_r Q_b &= T(t)\varphi(s_b)ds_b \equiv T(t)ds_b; \\ \delta_r Q_c &= T(t)\varphi_c(s_a, s_b)dS_c \equiv T(t)dS_c, \end{aligned} \tag{1.8.3}$$

where we introduced a new differential form $dS \equiv \varphi(s)ds$, the function S is termed the *metrical entropy*. The above derivation provides no guidance on how to select a suitable function to represent $T(t)$. We are thus allowed to identify T with the thermodynamic temperature scale introduced in Section 1.2. This step is validated by arguments supplied in Section 1.12, and particularly, in Section 2.4.

Implicit in the above derivation is the assumption that reversible conditions prevail during the heat exchange process. Otherwise, it would not have been possible to describe the operations with a limited number of well-defined, equilibrium thermodynamic variables x_i or y_i . We therefore express the second law in the final form

$$dS = \delta_r Q/T, \tag{1.8.4}$$

which thus differs from the first law in its range of applicability. The second law is to be supplemented by one other fundamental assertion:

The entropy of the final state for a process occurring in an isolated system is never less than that of the initial state.

Implicit in this statement is the idea that processes in isolated systems are not subject to experimental control and therefore are spontaneous. For such changes, the entropy continues to increase until equilibrium is established, at which point the entropy of the system is at a maximum, consistent with the imposed constraints that lead to the properties of the system in its final state. Nevertheless, it is always possible to decrease the entropy of a system by breaking the isolation through appropriate interactions with the surroundings. If these are executed irreversibly, there must occur elsewhere in the universe a compensating process such that the total entropy of the universe does increase.

One need not be concerned about detailing the events taking place during an irreversible process. It is only necessary to establish that the system remain equilibrated at the beginning and at the end of the process, so that the overall change in state of the system can be characterized by a limited number of thermodynamic variables.

Final Comments

At this stage, we write down the fundamental formulation that specifies the energy of a system in differential form, by combining the first and second laws as follows: When only mechanical and chemical work is incurred *and all processes are carried out reversibly*, we may introduce Eqs. (1.8.4), (1.5.3b), and (1.5.9) to write

$$dE = \delta_r Q + \delta_r W = TdS - PdV + \sum_{i=1}^c \mu_i dn_i. \quad (1.8.5)$$

This is the fundamental starting point for many subsequent thermodynamic operations. For other types of work, appropriate differential forms need to be included on the right; many such examples are provided in due time. Note that E has been expressed in terms of another function of state S , as well as by directly measurable changes in volume and composition. Later we find ways to reexpress dS in terms of measurable control variables. At the risk of nauseous repetition, note that the differential forms on the right specify reversible entropy, volume, and compositional alterations of the energy due to interactions with the surroundings. Purely internal processes that change the entropy do not involve interactions with the surroundings; they are then irreversible, do not change the energy, and are therefore not included here in dS . Such internal changes are covered in Section 1.16, and are handled as shown in Section 1.9.

Finally, a closing remark: other equivalent statements of the second law are commonly cited, namely those of Kelvin and Planck; these are based on the operation of heat engines, discussed in Section 1.11. For more information, see Note 2.

A Second Parable

Just as for the first law, one may provide a parable that illuminates the second law of thermodynamics and its consequences; we follow the presentation by Spalding and Cole.⁵ Entropy change may be likened to a difference ΔS_{AB} in elevation between two points A and B in rough, mountainous terrain. A mountaineer elects to measure ΔS_{AB} in terms of the number of steps, $n \equiv n_r$, each 1 ft in height, he must take to get from level A to level B. On a firm path, the difference in height is then given by $\Delta S_{AB} = n_r$. But if he chooses a slippery path through the underbrush filled with dirt and gravel, slippage occurs at every step. Now, given a particular height difference, he fails to surmount this difference with the number of 1 ft incremental steps, $n \equiv n_i$, that would have sufficed had he stayed on

the firm path: here $\Delta S_{AB} > n_i$. Considerable effort has been wasted in the form of heat supplied to the countryside when the climber, dirt, and gravel resettle at every step. Furthermore, rather than by counting n_r , the value of ΔS_{AB} may be ascertained by consulting geodetic maps on which altitude contours are entered.

It should be clear that ΔS_{AB} corresponds to an entropy change and that n_r and n_i simulate $\int \dot{d}_r Q/T$ and $\int \dot{d}_i Q/T$, respectively, while contour lines on a map correspond to tabulations of entropy values.

Statistical Interpretation of the Entropy Function

We end with a brief exposition concerning the statistical interpretation of the entropy function. For a brief review of the fundamental concepts, see Chapter 10 and consult texts on statistical thermodynamics for an in-depth exposition.

The statistical formulation is based on the premise that the macroscopic properties of a system should be directly deducible from the properties, disposition, and interactions of the constituent particles (atoms, electrons, nuclei, etc.). Quantum mechanics furnishes the latter information in terms of the elementary statistics to which the particles are subject, and via the energy levels ε_i and their associated degeneracies g_i among which the particles are distributed. Each such distribution corresponds to a possible macroscopic manifestation of the system. At equilibrium, it is the most probable distribution that prevails overwhelmingly as compared to any other configuration, and that corresponds to the maximum entropy of the macroscopic system. Deviations from this configuration are inevitable; they come under the topic of fluctuations that are taken up in Section 1.17. However, the system away from equilibrium will spontaneously revert back to the most probable configuration.

The basic idea then is to link microscopic configurations to the entropy. This link is provided by the famous Boltzmann formula:

$$S = k_B \ln \Omega, \quad (1.8.6)$$

where k_B is the *Boltzmann's constant*, which is needed to satisfy the dimensionality requirements, and Ω is the probability of encountering the system in a microscopic state that must be specified as shown below. The above relation may be rationalized by noting that if Ω_A and Ω_B are the probabilities for two completely independent subsystems, A and B, that constitute the whole system, then the probabilities multiply: for the system as a whole $\Omega = \Omega_A \Omega_B$, while the entropies are additive. $S = S_A + S_B$. A more persuasive rationale is supplied in Section 10.2.

As shown in Chapter 10, in many cases the probability function of interest is given by the approximations

$$\Omega = N! \prod_i \frac{g_i^{n_i}}{n_i!} \quad \text{or} \quad \Omega = \prod_i \frac{g_i^{n_i}}{n_i!}, \quad (1.8.7)$$

for distinguishable or indistinguishable particles, respectively, that are placed in energy states labeled ε_i . Here g_i represents the degeneracy of energy level ε_i available to n_i elementary units assigned to the i th state; N represents the total number of particles. Entropy is thus seen to be a measure of the probability of encountering a state that is specified by a distribution such as Eq. (1.8.7).

In many discussions of the above topic, you encounter the statement that entropy is also a measure of the disorder in a system. As an example, consider a perfectly ordered configuration, such as two gases A and B completely separated in one container, is enormously less likely to be encountered than

a disordered state, in which A and B are intimately mixed to form a uniform composition. However, order and disorder in this context are subjective concepts, while probabilities are precise measures of states. We therefore will not pursue this idea further.

Correlation of Temperature, Energy, and Entropy

Before proceeding it may be instructive to have a first look at how the rather abstruse concepts of temperature, energy, and entropy can be linked to actual physical measurements. Early methodologies relied on changes in mechanical properties such as volume or pressure with alterations in the state of the system. Gases are much more responsive to such adjustments than condensed phases and were, therefore, extensively used. Since then, a large array of measurement techniques has actually been employed for this purpose. A partial sketchy survey of these techniques is provided by Figure 1.8.1, but for more than this incidental presentation, you are referred to special monographs on the subject.

In short, to quantify hotness levels and entropy changes, one can use noble gases and note their response to experimental changes. This involves the use of isothermals $t(P, V) = \text{const.}$ that derive from their equation of state, which was used in setting up the zeroth law of thermodynamics. The isentropics $s(P, V) = \text{const.}$ result from studying the quasistatic adiabatic processes considered in setting up the second law. The resulting absolute temperature, T , and metrical entropy, S , are as yet unknown functions of the adopted empirical functions t and s ; we seek to establish relations $T = \tau(t(P, V))$ and $S = \sigma(s(P, V))$ that link basic theory and experiment. For this purpose, we again introduce the formal expression $E = \epsilon(P, V)$ that links energy to the mechanical properties of the noble gas. Then from $TdS = dE + PdV$ it follows that at constant hotness levels

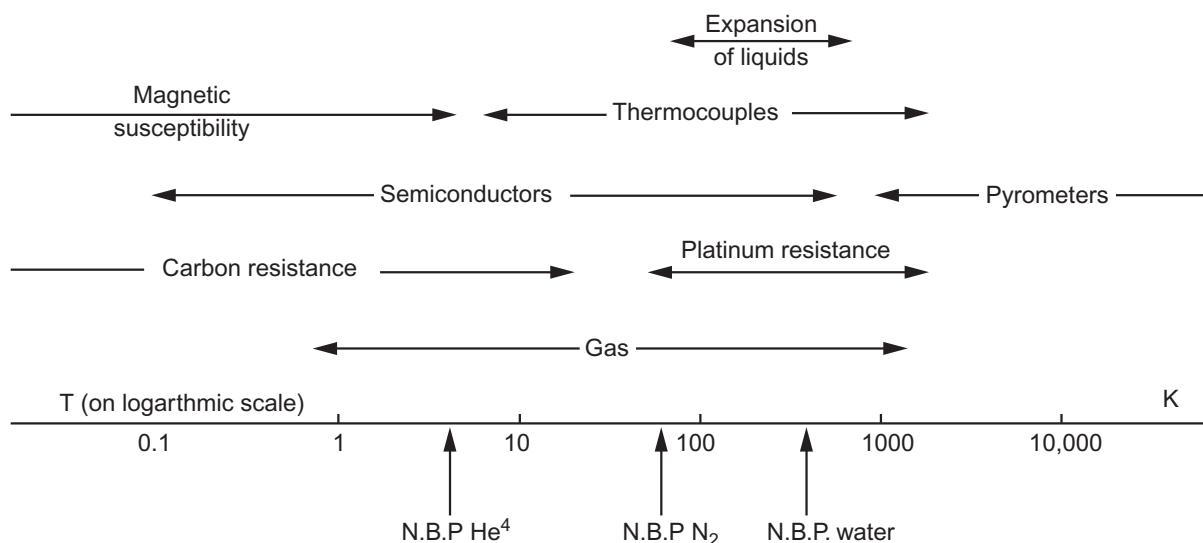


FIGURE 1.8.1

Sketch of the use of several thermometers over a range of temperatures.

$$\tau \left[t(P, V) \right] \frac{d\sigma}{ds} \left(\frac{\partial s}{\partial P} dP + \frac{\partial s}{\partial V} dV \right) = \frac{\partial \varepsilon}{\partial P} dP + \left(\frac{\partial \varepsilon}{\partial V} + P \right) dV. \quad (1.8.8)$$

Since P and V are independent variables, we can match coefficients, so that

$$\frac{\partial \varepsilon}{\partial P} = \tau \left[t(P, V) \right] \frac{d\sigma}{ds} \frac{\partial s}{\partial P} \quad (1.8.9a)$$

$$\frac{\partial \varepsilon}{\partial V} = \tau \left[t(P, V) \right] \frac{d\sigma}{ds} \frac{\partial s}{\partial V} - P. \quad (1.8.9b)$$

On introducing second derivatives we obtain

$$\frac{\partial^2 \varepsilon}{\partial V \partial P} = \frac{d\sigma}{ds} \left(\frac{d\tau}{dt} \frac{\partial t}{\partial V} \frac{\partial s}{\partial P} + \tau \frac{\partial^2 s}{\partial V \partial P} \right), \quad (1.8.10a)$$

$$\frac{\partial^2 \varepsilon}{\partial P \partial V} = \frac{d\sigma}{ds} \left(\frac{d\tau}{dt} \frac{\partial t}{\partial P} \frac{\partial s}{\partial V} + \tau \frac{\partial^2 s}{\partial P \partial V} \right) - 1. \quad (1.8.10b)$$

The two equations are equal; it follows that

$$\frac{d\tau}{dt} \frac{d\sigma}{ds} \left(\frac{\partial s}{\partial V} \frac{\partial t}{\partial P} - \frac{\partial s}{\partial P} \frac{\partial t}{\partial V} \right) = 1. \quad (1.8.11)$$

Eq. (1.8.11) indicates that whatever functions τ and σ are to be chosen, they must satisfy the above equation identically. For noble gases, He in particular, it is well established that the product PV is very nearly constant over a wide range of conditions, so long as the gas remains equilibrated with a reservoir at a fixed hotness level, and that it responds linearly to a succession of applied hotness levels. Hence, we can take PV to be a measure of hotness in terms of the empirical temperature t : this allows us to set $PV \equiv \tau = \tau(t)$. We are at liberty to choose any monotonically varying function of t as a measure of hotness levels; so, it makes sense to select the simplest function that may be contemplated in conformity with the use of noble gases, namely,

$$t = t(P, V) = PV, \quad (1.8.12)$$

where we can now replace PV by a quantity proportional to T , that we had linked to mechanical properties of an ideal gas in Section 1.2, and in step (7) of Eq. (1.8.3). This relation is then assumed to hold exactly for an ideal gas.

A similar argument may be employed to deal with the function s , based on the empirical observation that in an adiabatic expansion involving a noble gas the product PV^γ is nearly constant; γ is a fixed quantity (that turns out later to be the ratio of heat capacities at constant pressure and volume). By analogy to the preceding argument we, therefore, set up the following equation for the metrical entropy at constant hotness levels:

$$s = s(PV) = PV^\gamma. \quad (1.8.13)$$

Now use Eqs. (1.8.12) and (1.8.13) in Eq. (1.8.11) to find that

$$(\gamma - 1)s \frac{d\tau}{dt} \frac{d\sigma}{ds} = 1. \quad (1.8.14)$$

As may be verified by direct substitution, Eq. (1.8.14) is satisfied by setting

$$\frac{d\tau}{dt} = a; \quad \frac{d\sigma}{ds} = [(\gamma - 1)sa]^{-1}, \quad (1.8.15)$$

where a is an arbitrary constant that remains to be specified. Integration yields

$$\tau \equiv T = at + T_0 \quad (1.8.16)$$

$$\sigma \equiv S = \frac{1}{(\gamma - 1)a} \ln s + S_0, \quad (1.8.17)$$

where we reintroduced the metrical entropy S of Eq. (1.8.3) as the proper thermodynamic entity that deals with heat transfers (among other matters) and is thus linked to adiabatic processes. Eq. (1.8.17) applies to noble gases as working substances but becomes exact for ideal gases. T_0 and S_0 are parameters that must be determined separately.

Determination of Parameters

We determine various parameters by inserting Eqs. (1.8.16) and (1.8.17) in the relation $TdS = dE + PdV$, to find

$$TdS = (at + T_0) \frac{1}{(\gamma - 1)a} d \ln s. \quad (1.8.18)$$

The PdV term requires more manipulation. From Eqs. (1.8.13) and (1.8.14) we obtain $s = tV^{\gamma-1}$, whence

$$ds = t(\gamma - 1)V^{\gamma-2}dV + V^{\gamma-1}dt. \quad (1.8.19)$$

Solve this relation for

$$dV = t^{-1}(\gamma - 1)^{-1}V^{2-\gamma}ds - t^{-1}(\gamma - 1)^{-1}Vdt. \quad (1.8.20)$$

Introduce $s = tV^{\gamma-1}$ in the first term and $t = PV$ into the second to obtain

$$dV = (\gamma - 1)^{-1}Vs^{-1}ds - (\gamma - 1)^{-1}P^{-1}dt, \quad (1.8.21)$$

so that finally

$$PdV = (\gamma - 1)^{-1}t d \ln s - (\gamma - 1)^{-1}dt. \quad (1.8.22)$$

Next, insert Eqs. (1.8.18) and (1.8.22) into $dE = TdS + PdV$ to obtain

$$dE = (\gamma - 1)^{-1}[dt + (T_0/a)d \ln s], \quad (1.8.23)$$

which may be integrated to yield

$$E = (\gamma - 1)^{-1}[t + (T_0/a) \ln s] + E_0. \quad (1.8.24)$$

Conclusion

At this point we invoke another experimental fact: over a wide temperature range noble gases approximately obey the relation $(\partial E / \partial V)_t = 0$. This relation is assumed to hold exactly for an ideal gas. Now, as specified by Eq. (1.8.21), s is a function of V , so that as it stands, Eq. (1.8.24) for the energy does involve V . Therefore consistency with $(\partial E / \partial V)_t = 0$ can be achieved only by setting $T_0 = 0$. Then Eq. (1.8.16) reduces to

$$T = at = aPV. \quad (1.8.25)$$

Clearly, then, for an ideal gas $a^{-1} = nR$, which leads to the specification of T in terms of the pressure and volume of an ideal gas.

Furthermore, Eq. (1.8.24) now reads

$$E = (\gamma - 1)^{-1} nRT + E_0, \quad (1.8.26)$$

where we later show that $(\gamma - 1)^{-1} nR \equiv C_V$ is the heat capacity at constant volume; right now C_V is simply a shorthand notation for the indicated symbols on the left. Relative to an arbitrary energy constant E_0 , we have been able to specify the energy in terms of the temperature T and the γ parameter, as in Eq. (1.8.26).

Next, Eq. (1.8.17) may be combined with Eq. (1.8.14) to yield

$$S = C_V \ln s + S_0 = C_V(\ln P + \gamma \ln V) + S_0. \quad (1.8.27)$$

Since $P = a^{-1} V^{-1} T$, then, $\ln P = -\ln a - \ln V + \ln T$, and since

$$C_V \ln P + \gamma C_V \ln V = -C_V \ln a + C_V \ln T + C_V(\gamma - 1) \ln V, \quad (1.8.28)$$

we obtain another result of interest:

$$S = C_V \ln T + a^{-1} \ln V + (S_0 - C_V \ln a) \equiv C_V \ln T + nR \ln V + S'_0, \quad (1.8.29)$$

which shows how the entropy can be determined experimentally in terms of measurable quantities.

By way of review, the above relations have shown how to construct a thermodynamic temperature scale, T , the energy, E , and the entropy, S , based on the empirical relations that involve the pressure and volume of an ideal gas. All of this foreshadows material that is presented later. Actually, part of the previously used procedure is independent of the choice of a working material, as is established by verifying that a different working material with properties $t' = t'(P, V)$, $s' = s'(P, V)$ can be introduced to construct $T = \tau'(t'(P, V))$ and $S = \sigma'(s'(P, V))$. This again leads to a relation of the form (1.8.11). It is this flexibility that enables many different pressure and volumes as determined by empirical measurement systems to be correlated with the thermodynamic temperature scale and with the entropy of the system contemplated for their use.

Footnotes and Query

- 1.8.1. We follow here the presentation provided by H.A. Buchdahl, *The Concepts of Classical Thermodynamics* (Cambridge University Press, 1966) Chapters 5, 6. If you are interested in a greatly expanded procedure and in a detailed exposition of Carathéodory's elegant approach, read Chapter 9.
- 1.8.2. The *Kelvin* and *Planck* statements of the second law (Section 1.11) deal with the impossibility of operating thermal engines under certain prescribed conditions; from these assumptions, the second law may then be deduced. There is no logical objection to such a procedure, but it does seem somewhat unsatisfactory to base a universally applicable law on principles pertaining to the operation of heat engines. The reverse procedure, outlined in Section 1.11 does provide what appears to be a better alternative; here the characteristics of cyclically operated heat engines are derived as a consequence of the second law.
- 1.8.3. Is a process for which $dS = 0$ necessarily adiabatic? Explain your reasoning.

- 1.8.4. In consultation with Section 1.11 provide reasons why it is almost inevitable that one should select the thermodynamic temperature scale as the one for use in identifying the integrating denominator.
- 1.8.5. D.B. Spalding and E.H. Cole, *Engineering Thermodynamics* (Arnold, London, and McGraw-Hill, New York, 1959).
- 1.8.6. Explore the shortcomings of this parable.

1.9 Consequences of the First and Second Laws

Preliminaries

In this section, we lay the foundations for all subsequent thermodynamic investigations that are based on the first and second laws.¹ This finally gets us to a point where we can learn how thermodynamics can actually be used! Here we set up a variety of functions of state to study of systems under different sets of operating conditions. The derivations involve the interactions of a system with its surroundings, this combination being treated as an isolated unit. Our further treatment of both reversible and irreversible processes hinges on one crucial assumption: the surroundings are taken to be so large and kept so well mixed that all processes inside its boundaries occur reversibly, even in its interactions with a system that operates irreversibly. In the absence of this fundamental tenet, specialized mathematical techniques are required to handle irreversible phenomena. Further, the surroundings are generally supposed to be so large that all its *intensive variables* remain unaltered during the interactions with the attached system. (Think of a nuclear reactor facility for which the ocean is used as a thermal reservoir.)

We first need to investigate what is meant by the “temperature” of a system undergoing irreversible changes. One possible scenario is depicted in Figure 1.9.1. A system at an essentially uniform temperature T is thermally coupled to surroundings at the essentially uniform temperature T_0 . The two are separated by an intervening, moveable thin barrier, consisting of a poor thermal conductor. During any heat exchange, the two different temperatures remain well defined over most of the two domains; the changeover from T_0 to T occurs almost entirely at the narrow interface region. If the heat transfer takes place at a sufficiently slow rate, while keeping T_0 constant, T can be changed uniformly, whereby we maintain the concept of temperature under nonequilibrium conditions. In principle, there is no limit to

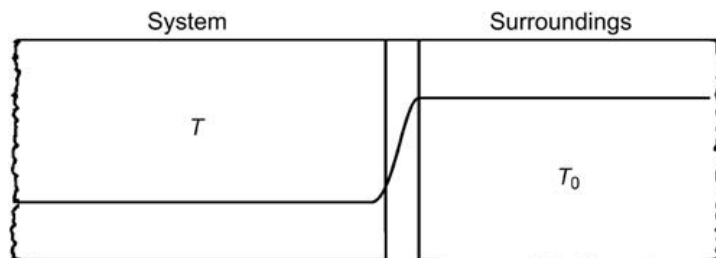


FIGURE 1.9.1

Temperature profile near the junction between a system (left) at temperature T and a reservoir (right) at temperature T_0 under QSI operating conditions. The change in temperature occurs over a narrow boundary region.

the temperature difference that may thus be maintained. Such changes will be termed *quasi-static irreversible processes* (QSIPs) across the junction between the systems and its surroundings. Obviously, processes of this type are best approximated by working with materials that have a fast relaxation time, and by a system that is very thin in its lateral extension. Alternatively, one may surround a dispersed version of the system by a multiplicity of reservoirs acting in concert.

Other methods of dealing with nonuniform temperatures are in common use, for example, through the replacement of T by its average taken over the extension of the system.² Or, the temperature T may be taken as a function of position within the sample; the analysis then invokes the methodology of irreversible phenomena, detailed in Chapter 6. However, no matter what method is adopted, the temperature concept becomes problematic at sufficiently large departures from equilibrium, as, for example, in systems exhibiting turbulence.

Analogous remarks apply to all other intensive variables, such as pressure or chemical potential.

Entropy Changes

We begin our fundamental study by examining the entropy changes in an isolated compound unit: one component comprises the reservoir, the other, the system. Both remain at fixed volume and composition, no other forms of work being allowed. Consider an infinitesimal step of a particular process that takes the system from state A to state B via an exchange of heat. Let this step first be carried out *reversibly*, with a corresponding entropy change, $d_a S_u$ in the universe; this is the sum of the entropy change dS of the system and the entropy change $d_a S_0$ of the surroundings while both are held at the common temperature T (actually, in the limit where the temperature difference between the system and surroundings approaches zero). According to the second law, there is no net change in the total entropy of the universe; thus,

$$d_a S_u \equiv dS(T, V, n_i) + d_a S_0(T, V_0, n_{0i}) = 0. \quad (1.9.1a)$$

Next, let the same step within the system at temperature T be carried out irreversibly, while the reservoir is held at temperature T_0 . Since entropy is a function of state of the system, $dS(T, V, n_i)$ is the same as before, but the entropy change in the surroundings, here designated $d_b S_0(T_0, V_0, n_{0i})$, is now different. According to the second law, the entropy of the universe can only increase, so that

$$d_b S_u \equiv dS(T, V, n_i) + d_b S_0(T_0, V_0, n_{0i}) > 0. \quad (1.9.1b)$$

The use of inequalities is always awkward; we shall avoid many problems by introducing an *entropy deficit function* $\delta\theta > 0$ that converts Eq. (1.9.1b) into an equality:

$$d_b S_u \equiv dS(T, V, n_i) + d_b S_0(T_0, V_0, n_{0i}) - \delta\theta = 0. \quad (1.9.1c)$$

Here $\delta\theta$ is simply a book-keeping device. However, it acquires meaning when we subtract Eq. (1.9.1a) from Eq. (1.9.1c) to obtain

$$d_b S_0(T_0, V_0, n_{0i}) - d_a S_0(T, V_0, n_{0i}) = \delta\theta, \quad (1.9.1d)$$

which shows that $\delta\theta$ represents the entropy difference in the surroundings when the infinitesimal step within the system is carried out irreversibly as opposed to reversibly. Moreover, since the system + surroundings form a closed unit, any infinitesimal heat³ ($\delta_i Q$) lost (gained) by the system operating at temperature T is gained (lost) by the surroundings ($\delta_r Q_0$) operating reversibly at temperature T_0 . Thus, necessarily, $-\delta_i Q = \delta_r Q_0$. It is only in the limit $T - T_0 \rightarrow 0$ that the heat transfer from or to the system can be carried out reversibly.

During the reversible step (r) at the common temperature T , the infinitesimal entropy change of the *system* is given by $dS \equiv d_r S = \delta_r Q/T$; hence, by Eq. (1.9.1a), the entropy change in the *surroundings* is given by

$$d_a S_0 = -dS = -\delta_r Q/T. \quad (1.9.2a)$$

For the same step executed irreversibly (i), with the temperature of the system at T and that of the surroundings at T_0 , the resulting heat exchange $\delta_i Q = -\delta_r Q_0$ produces an entropy change in the *surroundings* specified by

$$d_b S_0 = \delta_r Q_0/T_0 = -\delta_i Q/T_0, \quad (1.9.2b)$$

where we invoked the reversibility of all processes in the reservoir. On inserting Eqs. (1.9.2a) and (1.9.2b) into Eq. (1.9.1d), we obtain the fundamental relation

$$\delta_i Q = (T_0/T)\delta_r Q - T_0 d\theta = T_0(dS - d\theta) < (T_0/T)\delta_r Q. \quad (1.9.3a)$$

The inequality is self-evident for the case where heat is transferred into the system; here $\delta_i Q$ and $\delta_r Q$ are both positive with $T < T_0$. Moreover, this result must apply for any value $T < T_0$, and particularly, to the limiting case $T = T_0$. One thereby obtains a tighter constraint, as a string of inequalities:

$$\delta_i Q < \delta_r Q < (T_0/T)\delta_r Q, \quad (1.9.3b)$$

where the first statement is a version of the *Clausius inequality*. Implicit in the above is the assumption that in the limiting case, $d\theta$ does not necessarily vanish: as an example, consider the case where the reversible heating of the system triggers a spontaneous reaction totally within the sample.

When heat is transferred out of the system, with $T > T_0$, Eq. (1.9.3a) then shows that $\delta_i Q$ is more negative than $(T_0/T)\delta_r Q$. This result applies as well to any $T > T_0$, and thus, to the limiting case $T = T_0$. We then recover a string of increasingly less negative quantities going from left to right in Eq. (1.9.3b).

Equation (1.9.3a) may be restated in the equivalent form

$$\delta_i Q = \delta_r Q + (T_0/T - 1)\delta_r Q - T_0 d\theta, \quad (1.9.3c)$$

in which the last two terms directly take account of the difference between the heat transferred irreversibly in the infinitesimal step, $\delta_i Q$, and that transferred reversibly, $\delta_r Q$, in executing the same step.

When the temperature of the system and reservoir differ only infinitesimally $T \approx T_0$, Eq. (1.9.3c) reduces to⁴

$$\delta_i Q = \delta_r Q - T d\theta = T(dS - d\theta). \quad (1.9.3d)$$

Here $T d\theta$ may be interpreted as the difference in heat transfers executed reversibly and irreversibly under these limited conditions. As already explained, this may happen if an otherwise reversible heat transfer into the system triggers additional irreversible phenomena totally within the system. Equation (1.9.3d) shows directly that the irreversible heat transfer is less positive or more negative than its reversible counterpart, when heat is absorbed or released by the system.

One may also turn Eq. (1.9.3a) around to read

$$dS = \delta_i Q/T_0 + d\theta \leq \delta_i Q/T_0, \quad (1.9.3e)$$

which shows explicitly that in irreversible processes, the total entropy change in the system is only partially accounted for by the transfer of heat. Note that it is the well-established temperature of the reservoir that always enters the expression. The above should be contrasted with the usual relation $dS = \delta_r Q/T$, in which the entropy change is completely tracked by the reversible heat transfer at the common temperature T . Equation (1.9.3e) represents the *Clausius inequality*.

Equation (1.9.3e) merits further careful scrutiny. In the above infinitesimal step that carries the system from state A to state B, dS is always the *total* concomitant entropy change. In the absence of any work or compositional changes, the only channel for outside communication is the transfer of heat, as shown by the first term on the right. This then dictates that the $\delta\theta$ term represents the additional contribution to dS arising from purely *internal reconfigurations* of the system that are outside the control of the experimenter.

While interesting in its own right, Eq. (1.9.3e) becomes useful only after it is shown how to specify $\delta\theta$ in terms of experimentally measurable quantities. This matter is attended to below.

An important confirmation of the above procedure is found by examining adiabatic processes that occur in isolation; for such cases, Eq. (1.9.3e) reduces to

$$\delta S = \delta\theta > 0, \quad (1.9.3f)$$

where the δ symbol serves as a reminder of the special conditions that prevail. This equation shows that processes proceeding without outside intervention (after release of a constraint) always increase the entropy of the system. Successive increments produce a monotonic entropy increase until the spontaneous process has run its course. At that point, a state of maximum entropy has been reached, with $\delta S = 0$, subject to whatever constraints still apply. This is the content of the famous dictum by Clausius that the entropy of the world (nowadays, we would say, of our universe) tends toward a maximum.

A nontrivial lower bound on $\delta\theta$ is found by applying the $\delta_i Q < \delta_r Q$ inequality to Eq. (1.9.3c). This requires that the last two terms on the right be negative, whence we find that

$$\delta\theta > (T_0/T - 1)\delta_r Q/T_0 > 0. \quad (1.9.3g)$$

Here the right-hand side is always positive. For, when $T < T_0$ ($T > T_0$), heat flows from the reservoir (system) into the system (reservoir), and $\delta_r Q$ is positive (negative), as is, respectively, the quantity $(T_0/T - 1)$. Thus, $\delta\theta$ has as its lower bound the quantity in the middle, which exceeds zero when T and T_0 differ. Equation (1.9.3g) then yields useful information on the bounds for $\delta\theta$ in terms of experimentally determinable variables T , T_0 , and $\delta_r Q$ (or dS).

Performance of Work

Next, we reintroduce the first law of thermodynamics. Because the energy E is a function of state, we set

$$dE = \delta_r Q + \delta_r W = \delta_i Q + \delta_i W, \quad (1.9.4a)$$

where W is the work performed during the process. On eliminating $\delta_i Q$ between Eqs. (1.9.3c) and (1.9.4a), we may solve for

$$\delta_i W = \delta_r W - (T_0/T - 1)\delta_r Q + T_0\delta\theta = \delta_r W - (T_0 - T)dS + \delta\epsilon, \quad (1.9.4b)$$

where $T_0 d\theta \equiv d\epsilon$ represents the infinitesimal difference in work performance under reversible as opposed to irreversible conditions. A special case of interest involves processes that are carried out under conditions where T and T_0 differ only infinitesimally, so that

$$d_i W = d_r W + T_0 d\theta \equiv d_r W + d\epsilon. \quad (1.9.4c)$$

We now note that the last two terms on the right in Eq. (1.9.4b) differ in sign from those in Eq. (1.9.3c) and therefore are positive. This leads to the inequality

$$d_i W > d_r W, \quad (1.9.4d)$$

which indicates, in accord with intuition, that work executed in carrying out a particular process irreversibly always exceeds that carried out reversibly, no matter what type of work is involved, or whether work is done on or by the system. In the latter case, less useful work is obtained from the system operating irreversibly.

Another significant feature of the present analysis is found by solving Eq. (1.9.4b) for

$$d\theta = (d_i W - d_r W)/T_0 + (1 - T/T_0)dS. \quad (1.9.5)$$

This relation expresses the contribution of irreversible phenomena to the infinitesimal entropy change, in terms of quantities that may be measured or calculated. It requires monitoring the entropy change in the system while carrying out a given process reversibly; heat capacity measurements may be used for this purpose, as shown in Section 1.15. Also, one needs to determine the work required for executing the same change reversibly and irreversibly, equivalent to noting by how much a given weight changes height in the earth's gravitational field in the two processes. Work executed in any given process may always be determined experimentally; the work involved in a reversible process may be calculated. Thus, the right-hand side of Eq. (1.9.5) is experimentally accessible.

Construction of Functions of State and their Extremal Properties

We now establish the basis of all subsequent thermodynamic developments, namely, the construction of appropriate functions of state. Recall that; then, using Eq. (1.9.3e), we obtain the fundamental expression

$$T_0 dS - d\epsilon + d_i W - dE = 0, \quad (1.9.6)$$

which makes no explicit reference to heat transfers but involves only the performance of work and irreversibility effects. Again, it is the well-established temperature of the surroundings that enters the equation. We now impose a series of special conditions on the system at temperature T that is enveloped by surroundings at a temperature T_0 . Let us initiate virtual displacements away from the equilibrium state, *while maintaining all initially specified constraints* and then examine the response of the system. As is customary, we introduce the symbol δ whenever such constrained variations are considered.

Isolated or Isoenergetic Systems

As a first example, consider an isolated system at temperature T for which $\delta_i Q = \delta_i W = \delta E = 0$. Then Eq. (1.9.6) reduces to

$$T\delta S = \delta\epsilon \equiv T\delta\theta \geq 0. \quad (1.9.7a)$$

Here, $\delta S \equiv \delta\theta \geq 0$ is the entropy change arising from irreversible processes occurring within a completely closed system. According to Eq. (1.9.7a), S can then only increase. After these processes have ceased, $\delta\theta \equiv \delta S = 0$, so that S has assumed an extremal value, which is maximum under the present constraints. To determine the above entropy change, one may repeat the same process under controlled, essentially reversible conditions. All this, of course, merely repeats what has been stated earlier in several guises.

Consider next an *isoenergetic* process for which $\delta E = 0$, but for which interactions between system and surroundings are permitted, such that the work exchange at each infinitesimal step is precisely balanced by a compensating heat exchange. This requires imposing quasi-equilibrium conditions so as to exclude irreversible phenomena over which an experimenter has no control. As a necessary condition, the temperatures of the system and surroundings differ only infinitesimally. We therefore set $\delta_r W = -\delta_r Q$ and $\delta\epsilon = 0$. Then Eq. (1.9.6) reduces to

$$T\delta S = \delta_r Q, \quad (1.9.7b)$$

which merely repeats the well-established fact that the entropy change is tracked by the reversible heat transfer. So far, nothing new.

Alternatively, we write

$$T\delta S = -\delta_r W, \quad (1.9.7c)$$

which indicates that one may reduce the entropy by the performance of work, $\delta_r W > 0$, on the system, while maintaining constant energy by a compensating heat transfer. This should dispel the idea that in any process whatever, the entropy of a system always remains either constant or can only increase.

State Functions for Isothermal Processes

At this stage, we enlarge on the set of useful state functions. Consider first events that are forced to take place *isothermally*, that is, in the limit: $\delta T = 0$ or $T_0 = T$. Then, using Eq. (1.9.4c), we combine $T\delta S$ and $-dE$ into one unit to rewrite Eq. (1.9.6) as

$$\delta(E - TS) \equiv \delta A = \delta_i W - \delta\epsilon - \delta_r W. \quad (1.9.8a)$$

We have thereby invented a new function of state, $A \equiv E - TS$, involving state functions on the right that had been previously introduced. A is called the *Helmholtz (free) energy* function. As indicated, changes in A are tracked by the reversible performance of work at constant T . If no work is involved, but irreversible (and therefore, uncontrollable) processes nevertheless take place within the system at constant temperature, we find that

$$\delta A = -\delta\epsilon \leq 0. \quad (1.9.8b)$$

Thus, irreversible processes in isolation at constant temperature lead to a decrease in its Helmholtz free energy. When quiescence sets in, $\delta A = 0$, and A is minimized; this characterizes the equilibrium constraint for an isolated system at constant temperature.

Here and later on we distinguish between mechanical and nonmechanical work by setting $\delta_i W = \delta_i W_m + \delta_i W_n$ and $\delta\epsilon = \delta\epsilon_m + \delta\epsilon_n$. In the exercises,⁵ you are asked to show that $\delta\epsilon_m$ and $\delta\epsilon_n$ must separately be nonnegative. Thus, if, in addition to T , the volume V is held fixed (*isothermal–isochoric* conditions, for which no mechanical work is possible), then the above expressions reduce to

$$\delta A = \delta_i W_n - \delta \varepsilon_n = \delta_r W_n. \quad (1.9.9)$$

Equation (1.9.9) is a restricted version of Eq. (1.9.8); contrary to some assertions in the literature, there is no need to require constant volume conditions to prove that under the stated conditions, A is a minimum at equilibrium.

As a different set of constraints, consider processes that take place within a system at constant temperature and pressure (*isothermal–isobaric conditions*). It is then expedient to collect E , TS , and PV as a unit and to rewrite⁶ Eq. (1.9.6) in the form $dE - d(TS) + d(pv) - \delta_i W_n + \delta \varepsilon_n = 0$, or

$$\delta(E - TS + PV) \equiv \delta G = \delta_i W_n - \delta \varepsilon_n = \delta_r W_n. \quad (1.9.10a)$$

By arguments now familiar, we have introduced a new function of state, $G \equiv E - TS + PV = A + PV$, the *Gibbs (free) energy*, involving the indicated combination of other functions of state. As is evident, changes in this quantity may be monitored by the reversible performance of work other than mechanical at constant T and P . Moreover, if in the isolated system irreversible phenomena occur under such isothermal–isobaric conditions,

$$\delta G = -\delta \varepsilon_n \leq 0, \quad (1.9.10b)$$

showing that in such circumstances, the Gibbs free energy of the system diminishes and reaches a minimum at equilibrium.

Isentropic Processes

We next consider *isentropic* processes that do not *explicitly* involve temperature as a variable. Here S is held invariant,⁶ and all processes involving Eq. (1.9.6) are subject to the restriction $dE + \delta \varepsilon - \delta_i W = 0$. Operating processes reversibly constitutes a sufficient condition for maintaining constant entropy, but in the execution of irreversible processes, heat flows must be allowed that maintain the system at constant entropy. Thus,⁶

$$\delta E = -\delta \varepsilon + \delta_i W = \delta_r W, \quad (1.9.11a)$$

showing that energy changes may be tracked by reversible performance of work under adiabatic conditions. This, of course, is simply a special case of the first law. The right-hand side involves Eq. (1.9.4b). However, if irreversible conditions prevail within the system in the absence of any work, we find

$$\delta E = -\delta \varepsilon \leq 0, \quad (1.9.11b)$$

so that as established earlier, under the stipulated conditions, the energy of the isolated system diminishes while the process lasts, and E is minimized at equilibrium.

A special case arises if the volume is also held fixed; under such *isentropic–isochoric* conditions,

$$\delta E = -\delta \varepsilon_n + \delta_i W_n = \delta_r W_n, \quad (1.9.12a)$$

and

$$\delta E = -\delta \varepsilon_n \leq 0. \quad (1.9.12b)$$

On the other hand, if pressure is kept fixed at constant entropy, we find for *isentropic–isobaric* conditions⁷ that $dE + d(PV) + \delta \varepsilon_n - \delta_i W_n = 0$, so that

$$\delta(E + PV) \equiv \delta H = \delta_i W_n - \delta \epsilon_n = \delta_r W_n. \quad (1.9.13a)$$

We thus encounter yet another function of state, the *enthalpy*, $H \equiv E + PV$, whose change under adiabatic conditions is tracked by reversible performance of nonmechanical work. When irreversible effects take place in the isolated system,

$$\delta H = -\delta \epsilon_n \leq 0, \quad (1.9.13b)$$

showing that this function too diminishes when the system is subjected to isentropic irreversible processes in the absence of work performance. At equilibrium, the enthalpy is a minimum.

SUMMARY

The full benefit of the functions of state listed above can become apparent only later. It bears repeating that functions of state are of enormous utility in the characterization of processes; for, they dispense with the need to deal with path-dependent quantities. For now we note that changes in A and G may be specified by reversible performance of work under isothermal conditions, while changes in E and H are usefully linked to performance of work under conditions of constant entropy. Variations in S may be similarly monitored under conditions of no energy change. This provides considerable flexibility in studying processes under different sets of experimental conditions, using only appropriate path-independent functions. Moreover, since work can always be measured empirically or calculated, these functions of state can be directly evaluated or determined experimentally in reversible processes.

Except for S , the above functions of state are all at a minimum when equilibrium prevails under the postulated constraints, while S is at a maximum. The above results are summarized in Table 1.9.I.

Table 1.9.I summarizes the conventional functions of state that are useful to specify equilibrium conditions under a variety of conditions in which mechanical work is involved. If experiments are carried out at other or additional sets of experimental conditions, new functions of state must be invented for that purpose, as is done in later chapters. The table should also put at rest a common misconception that the performance of work is invariably linked to energy changes. Also, we can illustrate the meaning of *virtual processes*. These refer to slight displacements of the system from equilibrium by imposing and then releasing an additional constraint while maintaining the original constraints. If the function of state does not change after such a displacement, the system is at equilibrium under the original constraints; if not, changes take place until a new equilibrium point is reached.

Table 1.9.I Characterization of Equilibrium

Fixed Parameters (Constraints)	Equilibrium	Relation to Reversible Work
E	$\delta S = 0$, S maximum	$\delta S = \delta_r W/T$
S	$\delta E = 0$, E minimum	$\delta E = \delta_r W$
S, V	$\delta E = 0$, E minimum	$\delta E = \delta_r W_n$
S, P	$\delta H = 0$, H minimum	$\delta H = \delta_r W_n$
T	$\delta A = 0$, A minimum	$\delta A = \delta_r W$
T, V	$\delta A = 0$, A minimum	$\delta A = \delta_r W_n$
T, P	$\delta G = 0$, G minimum	$\delta G = \delta_r W_n$

Remarks and Questions

- 1.9.1. The author is greatly indebted to Professor Dor Ben Amotz of Purdue University for many insightful discussions that have greatly clarified the fundamental concepts on which the present section is based. See also Dor Ben Amotz and J.M. Honig, *J. Chem. Phys.* **118**, 5932 (2003).
- 1.9.2. The question of how to deal with the concept of temperature in a system undergoing irreversible processes will also be raised in Chapter 6.
- 1.9.3. The notation is a bit awkward at this point: $\delta Q \equiv \delta_i Q$ really refers to the heat irreversibly released to (absorbed from) the surroundings, where it is reversibly absorbed into (released from) the reservoir. Since no heat escapes the compound system, we may set $\delta Q = -\delta Q_0 \equiv -\delta_b Q_0$.
- 1.9.4. Of course this statement, and similar ones shown below, should be more carefully formulated. Since no heat transfer can occur without a temperature difference between the system and the surroundings, Eq. (1.9.3d) is to be interpreted as a limiting law wherein $\delta_r Q$ signifies the heat flow in the limit $T - T_0 \rightarrow 0$.
- 1.9.5. To show that the individual $\delta \varepsilon$ are nonnegative, consider some spontaneous process for which $\delta \varepsilon_m < 0$; and examine the consequences by comparing work performance in reversible and irreversible processes.
- 1.9.6. At this point, it is vital to distinguish between adiabatic and isentropic processes. In the former $\delta Q = 0$, so that by the first law $\delta_i W = \delta_r W$; for any given infinitesimal process, all types of work performance lead to the same energy differential, dE . In the isentropic case, the energy change does depend on how the work is executed in the process. If done irreversibly, the entropy $\delta \theta$ and any entropy generated thermally across the boundaries from other sources must be transferred out of the system by removal of the appropriate amounts of heat to the surroundings. Incidentally, one way of maintaining the $T = T_0$ requirement is through the contrived step of ramping the reservoir temperature up or down in step with the temperature of the system at each infinitesimal change of conditions, but it is best to focus attention on the requirement that $dS = 0$.
- 1.9.7. We implicitly note that $d(PV)$, like the other functions of state in Eq. (1.9.10a), represents the changes in the irreversibly executed infinitesimal step. The other types of work are classified as being nonmechanical.
- 1.9.8. The so-called *grand potential* function $J = A - G$ has occasionally been used to characterize thermodynamic states. Show under what conditions this quantity can be related to reversible performance of work and characterize the properties of this function when irreversible processes occur.
- 1.9.9. As another example that relates to comparisons between processes executed reversibly or irreversibly, consider at constant volume the conversion of hydrogen and oxygen into steam over a platinum catalyst, and compare this with the explosive conversion by an electric spark. Are any changes needed in the derivations?

1.10 Functions of State; Reprise

To become really useful, we now set up the various functions of state in terms of experimentally measurable parameters, such as changes in volume, temperature, pressure, composition, and the like.¹ This ultimately forms the basis for many subsequent derivations. Our study again deals with an interacting but otherwise isolated composite unit comprised of a system plus its surroundings under nonequilibrium conditions. The processes under study are limited to QSIPs as set forth in Section 1.9.

The Energy

We begin with the first law of thermodynamics as applied to the *surroundings*, whose properties are all designated by the subscript zero. Such processes are by fiat taking place reversibly; thus, we start with the relation $dE_0 = \delta_r Q_0 + \delta_r W_0$ and replace the differentials on the right-hand side. Consider now a process involving a change in volume, an exchange of heat, and an interchange in chemical species. We thus set $\delta_r Q_0 = T_0 dS_0$ and apply Eq. (1.8.5) for the energy differential under reversible operating conditions. This leads to the conventional expression

$$dE_0 = T_0 dS_0 - P_0 dV_0 + \sum_i \mu_{0i} dn_{0i}, \quad (1.10.1)$$

where P_0 is the prevailing pressure, V_0 is the volume, μ_{0i} is the chemical potential of species i , and n_{0i} is the corresponding mole number—all for the surroundings. Let the closed unit of system + surroundings be maintained at a constant volume.² In that event, when the isolated unit undergoes irreversible processes, the *system* is subject to the constraints $dE = -dE_0$, $dV_0 = -dV$, $dn_{0i} = -dn_i$. Further, in dealing with QSIPs, we set $dS_0 \equiv d_b S_0 = -dS + \delta\theta$ (Eq. (1.9.1d)). Then the energy differential of the *system* is given as

$$dE = T_0 dS - P_0 dV + \sum_i \mu_{0i} dn_i - T_0 \delta\theta. \quad (1.10.2a)$$

Notice that the intensive variables are those of the surroundings; they are therefore well defined even when processes within the system are irreversible. In reversible transfers, the last term drops out; the intensive variables are those of the system: T , P , and μ_i . Clarifying remarks concerning the above relation are supplied in Appendix A.

The extensive quantities dS , dV , and dn_i represent the control variables; $\delta\theta$ is determined as shown in Eq. (1.9.5) or by the expressions developed below. Hence, dE is always well defined, even under nonequilibrium operating conditions. If work other than mechanical is involved, appropriate terms must be added to Eq. (1.10.2a) in the same format as was done in Section 1.5: a product of an intensive variable appropriate to the relevant work reservoir, and corresponding extensive variable for the system proper. Examples of this procedure are supplied in later chapters. As a reminder, we assume that all intensive variables of the reservoir remain fixed.

It is instructive to rewrite Eq. (1.10.2a) in the form

$$dE = (T_0 - T)dS - (P_0 - P)dV + \sum_i (\mu_{0i} - \mu_i)dn_i + TdS - PdV + \sum_i \mu_i dn_i - T_0 \delta\theta, \quad (1.10.2b)$$

where the variables lacking the subscript zero refer to the system. Equation (1.10.2b) is the generalized version of the conventional energy differential. Three special situations are of interest:

Case (a). The infinitesimal step is executed reversibly,³ with $T = T_0, P = P_0, \mu_i = \mu_{0i}$ and $d\theta = 0$; then Eq. (1.10.2b) reduces to the standard form

$$dE = TdS - PdV + \sum_i \mu_i dn_i, \quad (1.10.2c)$$

which may always be used to determine energy changes of a system, provided one can set up a *reversible path* by which to bring the system from the initial to the final state.

Case (b). All relevant control variables—in this case S , V , and n_i —remain fixed, but some processes (e.g., chemical reactions not involving the n_i) nevertheless continue within the system. Such occurrences are not subject to external control and therefore are irreversible. The extra entropy so generated is transferred to the surroundings, so as maintain S for the system at a constant value. In that case, Eq. (1.10.2a) reduces to

$$\delta E = -T d\theta < 0, \quad (1.10.2d)$$

The energy of the system thus spontaneously diminishes, in agreement with earlier statements.

Case (c). In this particular application, by external intervention, one removes the system slightly from its quiescent state where $dS = dV = dn_i = 0$ (all i). The intervention is then terminated while still retaining the constraints. If, as a response, the system returns to its initial state, then $\delta E = 0$; i.e., the energy of the system has reached an extremum, because of Eq. (1.10.2d), a minimum, consistent with the original constraints. Otherwise uncontrolled processes take place until a new quiescent state is reached. This is yet another statement that the energy of an isolated system undergoing spontaneous processes decreases until an equilibrium configuration obtains under the existing constraints.

Last, since E is a function of state we may subtract Eq. (1.10.2c) from Eq. (1.10.2b) to obtain

$$T_0 d\theta = (T_0 - T)dS - (P_0 - P)dV + \sum_i (\mu_{0i} - \mu_i)dn_i. \quad (1.10.2e)$$

Since the quantities on the right are experimentally accessible, the above equation permits specifying $d\theta$ in terms of S , V , and n_i as the control variables.

However, in actual experiments, these may not be the applicable control variables; we therefore seek to develop alternative expressions for $d\theta$ in terms of different control parameters.

Before doing so, it is instructive to consider a special case for the above. Let a system undergo an infinitesimal process from state A to state B at constant volume and composition, and in the absence of other work. Equation (1.10.2a) then reduces to

$$dE = T_0 dS - T_0 d\theta. \quad (1.10.2f)$$

Here the energy change dE does not correspond to the total entropy change dS , because the entropy contributions $d\theta$ arising from purely internal irreversible processes have been subtracted out, leaving only the entropy changes associated with transfers across the boundaries of the system. This, of course, repeats the point endlessly emphasized before: energy changes can be effected only through transfers of heat and work across the boundaries of the system.

Concerning the use of Eq. (1.10.2c), in conformity with earlier statements, since Eq. (1.10.2c) relates only to reversible processes, while dS refers to the total entropy change. For irreversible processes Eq. (1.10.2a) or (1.10.2b) must be used. Similar caveats hold for the remaining differential equations for functions of state introduced below.

We now resume our study of other fundamental relationships.

The Helmholtz (Free) Energy

In a similar manner, we construct the Helmholtz energy by applying the definition $A = E - TS$ introduced in Section 1.9, which sensibly involves the temperature T of the system. This changes the independent variable from S to T . Using Eq. (1.10.2b), we then find that

$$dA = (T_0 - T)dS - (P_0 - P)dV + \sum_i (\mu_{0i} - \mu_i)dn_i - SdT - PdV + \sum_i \mu_i dn_i - T_0 d\theta. \quad (1.10.3a)$$

Now, as documented below in Section 1.12, $A = A(T, V, n_i)$ is supposed to involve temperature, volume, and composition as the control variables for the Helmholtz energy, whereas Eq. (1.10.3a) involves a mix of quantities. To achieve the desired change, we express the entropy in terms of the appropriate control variables by setting $S = S(T, V, n_i)$. This leads to the appropriate differential form

$$dS = \left(\frac{\partial S}{\partial T} \right)_{V, n_i} dT + \left(\frac{\partial S}{\partial V} \right)_{T, n_i} dV + \sum_i \left(\frac{\partial S}{\partial n_i} \right)_{T, V, n_{i \neq j}} dn_i. \quad (1.10.3b)$$

Substitution in Eq. (1.10.3a) then produces the expression

$$\begin{aligned} dA = (T_0 - T) \left[\left(\frac{\partial S}{\partial T} \right)_{V, n_i} dT + \left(\frac{\partial S}{\partial V} \right)_{T, n_i} dV + \sum_i \left(\frac{\partial S}{\partial n_i} \right)_{T, V, n_{i \neq j}} dn_i \right] \\ - (P_0 - P)dV + \sum_i (\mu_{0i} - \mu_i)dn_i - SdT - PdV + \sum_i \mu_i dn_i - T_0 d\theta. \end{aligned} \quad (1.10.3c)$$

The partial differentials in the above relation may be recast as follows:⁴ as will be established in Section 1.12 by independent arguments, one may set $(\partial S / \partial T)_{V, n_i} = C_V / T$, and $(\partial S / \partial V)_{T, n_i} = (\partial P / \partial T)_{V, n_i}$ where C_V is the heat capacity at constant volume and composition, and where the appropriate Maxwell relation has been introduced as the second relation. Next, set up the identity $(\partial P / \partial T)_{V, n_i} = -(\partial V / \partial T)_{P, n_i} / (\partial V / \partial P)_{T, n_i}$; also, replace the numerator and denominator by the definitions $-\alpha V$ and $-\beta V$, where α and β are the isobaric coefficient of expansion and the isothermal compressibility, respectively. Last, set $(\partial S / \partial n_i)_{T, V, n_{i \neq j}} \equiv \hat{S}_i$ as defining the differential entropy at constant temperature, volume, and composition of species i . In this revised notation, Eq. (1.10.3c) assumes the form

$$\begin{aligned} dA = (T_0 - T) \left[(C_V / T) dT + (\alpha / \beta) dV + \sum_i \hat{S}_i dn_i \right] - (P_0 - P) dV \\ + \sum_i (\mu_{0i} - \mu_i) dn_i - SdT - PdV + \sum_i \mu_i dn_i - T_0 d\theta. \end{aligned} \quad (1.10.3d)$$

The above equation specifies the differential of the Helmholtz function under nonequilibrium conditions, in terms of T , V , and n_i . The associated coefficients all involve measurable quantities.

Under constraint (a), in which a reversible process is carried out³ with $T = T_0$, $P = P_0$, $\mu_i = \mu_{0i}$, and $d\theta = 0$, the Helmholtz function reduces to the standard form indicated in Section 1.12:

$$dA = -SdT - PdV + \sum_i \mu_i dn_i. \quad (1.10.3e)$$

The above demonstrates explicitly that when T , V , and n_i serve as control variables, the Helmholtz free energy A is the relevant function of state.

Under constraint (b), we examine the case where changes occur even when all the control variables (T , V , and n_i in this case) are held fixed. Such changes (e.g., chemical processes totally within the system, not involving the n_i) are not subject to control, and therefore, irreversible. Equation (1.10.3c) then reduces to

$$\delta A = -T_0 d\theta < 0, \quad (1.10.3f)$$

showing that in these circumstances, the Helmholtz energy diminishes during the process. This is in agreement with earlier claims.

Under constraint (c), we deform the quiescent system by external intervention to an adjacent state under the restrictions $dT = dV = dn_i = 0$, and then release the intervention. As in the preceding discussion, if the system returns to its initial state, $\delta A = 0$; the Helmholtz energy is at an extremum, in fact, at a minimum, in an equilibrium state consistent with the indicated constraints.

Since A is a function of state, we may subtract Eq. (1.10.3e) from Eq. (1.10.3d) to find

$$T_0 d\theta = (T_0 - T) \left[\left(\frac{C_V}{T} \right) dT + \left(\frac{\alpha}{\beta} \right) dV + \sum_i \hat{S}_i dn_i \right] - (P_0 - P) dV + \sum_i (\mu_{0i} - \mu_i) dn_i, \quad (1.10.3g)$$

which provides a second scheme for determining the entropy deficit function, here in terms of T , V , and n_i as relevant experimental variables; all the coefficients involve measurable quantities.

The Gibbs (Free) Energy

Using by now familiar methodology we define, as earlier, the Gibbs energy by $G = E - TS + PV = A + PV$. When converted to differential form, and on insertion of Eq. (1.10.3a), we obtain

$$dG = (T_0 - T) dS - (P_0 - P) dV + \sum_i (\mu_{0i} - \mu_i) dn_i - S dT + V dP + \sum_i \mu_i dn_i - T_0 d\theta \quad (1.10.4a)$$

as the expression that holds under nonequilibrium conditions. However, the control variables in present circumstances, cited in Section 1.12, should be T , P , and composition. Therefore, following the earlier recipe, we must express the entropy in the form $S = S(T, P, n_i)$ and the volume as $V = V(T, P, n_i)$, with corresponding differentials for dS and dV . On inserting these in Eq. (1.10.4a), we obtain

$$\begin{aligned} dG = (T_0 - T) & \left[(\partial S / \partial T)_{P, n_i} dT + (\partial S / \partial P)_{T, n_i} dP + \sum_i (\partial S / \partial n_i)_{T, P, n_i} dn_i \right] \\ & - (P_0 - P) \left[(\partial V / \partial T)_{P, n_i} dT + (\partial V / \partial P)_{T, n_i} dP + \sum_i (\partial V / \partial n_i)_{T, P, n_{i \neq j}} dn_i \right] \\ & + \sum_i (\mu_{0i} - \mu_i) dn_i - S dT + V dP + \sum_i \mu_i dn_i - T_0 d\theta. \end{aligned} \quad (1.10.4b)$$

We next cite the independently derived results of Section 1.12; we introduce⁴ $(\partial S / \partial T)_{P, n_i} = C_P / T$, as well as the Maxwell relation $(\partial S / \partial P)_{T, n_i} = -(\partial V / \partial T)_{P, n_i}$, derived below. As before, the partial derivatives $-(\partial V / \partial P)_{T, n_i}$ and $(\partial V / \partial T)_{P, n_i}$ are specified by βV and by αV , respectively. Also, we introduce $(\partial S / \partial n_i)_{T, P, n_{i \neq j}}$ and $(\partial V / \partial n_i)_{T, P, n_{i \neq j}}$ to represent partial molal entropies \bar{S}_i and volumes \bar{V}_i that are again found by independent procedures developed later. We thus rewrite Eq. (1.10.4b) in the less unwieldy form

$$dG = (T_0 - T) \left[(C_P/T) dT - \alpha V dP + \sum_i d\bar{S}_i dn_i \right] - (P_0 - P) \left[\alpha V dT - \beta V dP + \sum_i \bar{V}_i dn_i \right] + \sum_i (\mu_{0i} - \mu_i) dn_i - S dT + V dP + \sum_i \mu_i dn_i - T_0 d\theta. \quad (1.10.4c)$$

Equation (1.10.4c) is a generalization of the conventional Gibbs function that applies to QSI processes.

We once more consider three cases. Under alternative (a), we obtain the standard form cited in Section 1.12,

$$dG = -S dT + V dP + \sum_i \mu_i dn_i, \quad (1.10.4d)$$

which shows that G is the function of state to use when T , V , and n_i are the applicable control variables.

Under alternative (b), we examine whether processes occur within the system even when the control variables are all fixed. If so,

$$\delta G = -T_0 d\theta < 0, \quad (1.10.4e)$$

showing that spontaneous processes occurring when the appropriate control variables are held constant, always diminish the Gibbs energy. The process continues until the spontaneous process has run its course, at which point G is at a minimum consistent with the imposed constraint.

Under alternative (c), we contemplate a displacement of the system in the familiar manner from its equilibrium value to an adjacent state under the constraints $dT = dP = dn_i = 0$, and then allow the system to respond when the additional constraint is relaxed. If the same initial state is reached, $\delta G = 0$; the Gibbs free energy is then at a minimum consistent with the imposed constraints.

When Eq. (1.10.4d) is subtracted from Eq. (1.10.4c), we obtain

$$T_0 d\theta = (T_0 - T) \left[(C_P/T) dT - \alpha V dP + \sum_i \bar{S}_i dn_i \right] - (P_0 - P) \left[\alpha V dT - \beta V dP + \sum_i \bar{V}_i dn_i \right] + \sum_i (\mu_{0i} - \mu) dn_i, \quad (1.10.4f)$$

which shows how one may determine the deficit function when T , P , and composition are the independent variables.

The Enthalpy

Last, we turn to the enthalpy $H = E + PV$. By the customary technique, we develop the differential form $dH = dE + P dV + V dP$, into which we then insert Eq. (1.10.2b). We obtain

$$dH = (T_0 - T) dS - (P_0 - P) dV + \sum_i (\mu_{0i} - \mu_i) dn_i + T dS + V dP + \sum_i \mu_i dn_i - T_0 d\theta. \quad (1.10.5a)$$

Since, according to Section 1.12, $H = H(S, P, n_i)$ it is S , P , and composition that should be regarded as control variables. We therefore write the volume first in the form $V = V(P, T, n_i)$. We next introduce the entropy as a function of the same variables: $S = S(P, T, n_i)$, which function we invert to read $T = T$

(S, P, n_i) . Last, we insert this expression into the equation of state: $V = V(P, T(S, P, n_i), n_i) \equiv V(S, P, n_i)$. On taking the differential of this latter relation, we find

$$dV = (\partial V / \partial S)_{P, n_i} dS + (\partial V / \partial P)_{S, n_i} dP + (\partial V / \partial n_i)_{S, P, n_{i \neq j}} dn_i. \quad (1.10.5b)$$

Then, substituting Eq. (1.10.5b) into Eq. (1.10.5a), we obtain

$$\begin{aligned} dH = (T_0 - T)dS - (P_0 - P) \left[(\partial V / \partial S)_{P, n_i} dS + (\partial V / \partial P)_{S, n_i} dP + \sum_i (\partial V / \partial n_i)_{S, P, n_{i \neq j}} dn_i \right] \\ + \sum_i (\mu_{0i} - \mu_i) dn_i + TdS + VdP + \sum_i \mu_i dn_i - T_0 d\theta. \end{aligned} \quad (1.10.5c)$$

This specifies the enthalpy change in an infinitesimal step under nonequilibrium conditions. Under constraint (a), Eq. (1.10.5c) reduces to the standard form developed in Section 1.12,

$$dH = TdS + VdP + \sum_i \mu_i dn_i, \quad (1.10.5d)$$

while under constraint (b), with $dP = dS = dn_i = 0$, we find that

$$\delta H = -T_0 d\theta < 0, \quad (1.10.5e)$$

where again we note that the enthalpy diminishes in any spontaneous process occurring under the indicated restrictions. Under category (c), we find that $\delta H = 0$; the enthalpy has reached a minimum consistent with the imposed constraints.

When Eq. (1.10.5d) is subtracted from Eq. (1.10.5c), we obtain

$$\begin{aligned} T_0 d\theta = (T_0 - T)dS - (P_0 - P) \left[(\partial V / \partial S)_{P, n_i} dS + (\partial V / \partial P)_{S, n_i} dP \right. \\ \left. + \sum_i (\partial S / \partial n_i)_{S, P, n_{i \neq j}} dn_i \right] + \sum_i (\mu_{0i} - \mu_i) dn_i, \end{aligned} \quad (1.10.5f)$$

which yields yet another formulation for the deficit function that applies when S , P , and n_i are the variables of interest.

The minima achieved by the above functions of state should be contrasted with the maximum that characterizes the entropy of an isolated system undergoing spontaneous processes.

Integration of the Deficit Function

So far all variants of the deficit functions have been presented in differential form. To obtain the total deficit function θ , some type of integration is required. By way of illustration in general terms, consider Eq. (1.10.4f); here we must specify how $T, P, V, \bar{S}_i, \bar{V}_i, \mu_i, n_i$ change in the irreversible process. The simplest procedure involves introducing t as a parameter and then specifying how the above variables evolve with t during the process. In Appendix B we provide a specific example.

To simplify matters, assume that we deal with a closed system, which allows us to drop the integrals over dn_i . As usual, we assume that T_0 and P_0 remain fixed. The trajectory of each remaining

variable must be specified as a function of time t , whose integration stretches over limits between the initial time t_i and the final time t_f of the process. We write

$$\begin{aligned} \theta = & \int_{t_i}^{t_f} \left(\frac{T_0 - T(t)}{T_0} \right) \frac{C_P(T(t))}{T(t)} \frac{dT}{dt} dt - \int_{t_i}^{t_f} \left(\frac{T_0 - T(t)}{T_0} \right) \alpha V(t) \frac{dP}{dt} dt \\ & - \int_{t_i}^{t_f} \left(\frac{P_0 - P(t)}{T_0} \right) \alpha V(t) \frac{dT}{dt} dt + \int_{t_i}^{t_f} \left(\frac{P_0 - P(t)}{T_0} \right) \beta V(t) \frac{dP}{dt} dt. \end{aligned} \quad (1.10.6)$$

We must now supply the functions to be used for $T(t)$, $P(t)$, etc. For the nitty gritty details, consult some of the recent literature⁵ and the appendix. It turns out that the quantities θ_T , θ_P , and θ_n derived from the integrals involving dT , dP , and dn individually differ with each assumed time variation, their sum $\theta_T + \theta_P + \theta_n$ is invariant. This reflects the fact that entropy is a function of state.

We can demonstrate how to proceed in general by adopting several simplifying assumptions. For example, begin by ignoring the dependence of C_P , αV , and βV on t ; then the first integral reads

$$C_P \int (1/T - 1/T_0) dT = C_P [\ln(T_f/T_i) - (1/T_0)(T_f - T_i)].$$

The last integral may be rewritten in the form

$$-(\beta V/T_0) \left[P_0(P_f - P_i) - (P_f^2 - P_i^2)/2 \right].$$

Thereby these two integrals have become path independent in this approximation. The two central integrals cannot be simplified in this fashion. To avoid handling such integrals, we might assume that T in the integrand $(1 - T/T_0)$ may sensibly be replaced by its average value $\bar{T} \approx (T_f - T_i)/2$; a similar strategy may be adopted for $P(t)$ in the third integral. This approximation is tenable, for example, when T never departs extensively from T_0 , so that $(1 - T/T_0)$ remains “small”. Then these two integrals reduce to $-\alpha V(1 - \bar{T}/T_0)(P_f - P_i)$ and $(\alpha V P_0/T_0)(1 - \bar{P}/P_0)(T_f - T_i)$, respectively. The integration has thus been completed, but the extent to which the above simplifications hold can only be decided by experiment. Here, the above serves as a short-circuiting example to show how equations such as Eqs. (1.10.2e), (1.10.3g), (1.10.4f) and (1.10.5f) describe contributions to the entropy of QSI processes. More generally, if the indicated simplifications are inapplicable, the full integration of Eq. (1.10.6) must be undertaken after the path of the irreversible process has been specified in each case.

Alternative Derivation

An alternative derivation of the fundamental expression for $d\theta$ may be of interest. In the isolated compound unit, and under the conditions stipulated earlier, also involving QSIPs, the energy of the system and surroundings are specified by

$$dE = TdS - PdV + \sum_i \mu_i dn_i; \quad dE_0 = T_0 dS_0 - P_0 dV_0 + \sum_i \mu_{0i} dn_{0i}. \quad (1.10.7)$$

Now add these two relations. For the isolated compound unit, $dE + dE_0 = 0$. Also, as long as the total volume is held fixed, $dV + dV_0 = 0$, conservation of matter requires that $dn_i + dn_{0i} = 0$. Finally, adopt Eq. (1.9.1d). We then obtain

$$T_0 d\theta = (T_0 - T)dS - (P_0 - P)dV + \sum_i (\mu_{0i} - \mu_i)dn_i \quad (1.10.8)$$

in agreement with Eq. (1.10.2e). From here, it is but a small step to expand dS and dV as discussed below in Eq. (1.10.3c) to arrive at Eq. (1.10.3d).

SUMMARY

In summary, in the last two sections, we have addressed the problem of handling irreversibilities by introducing a deficit function that converts the commonly encountered inequalities into equalities. What starts out as a book-keeping operation allows us, at any stage of a given process, to relate the infinitesimal heat and work transfers of an irreversible process to that of the corresponding reversible process. It is emphasized that $d\theta$ relates solely to the entropy changes due to internal reconfigurations of the system that do not contribute to changes in the energy.⁶ We have also extended, under the assumption of QSI processes, the ordinary differential forms for the various functions of state to cases where the intensive variables of the system differ to any arbitrary extent from those of the surroundings. This enables us to demonstrate in a simple manner that the commonly used functions of state assume extremal values at equilibrium. The differential deficit function may then be determined in terms of the applicable control variables. To obtain the integrated form of the deficit function requires the introduction of time t as a parameter to simulate the manner in which the temperature, volume, pressure, or composition of the system changes in the course of any physical process. This is then followed by integrations over the time variable. The details are illustrated in several articles;⁵ a specific example is included as Appendix B.

Last, in the earlier part of this section, we have expressed the second law of thermodynamics in a form analogous to the first law. Thus, complementary to the first law,

$$dE = dQ + dW, \quad (1.10.9a)$$

we can reformulate the second law in a similar, though unrelated, form

$$dS = dQ/T_0 + d\theta, \quad (1.10.9b)$$

which replaces the commonly cited inequality $dS \geq dQ/T$. The important point is that the quantity $d\theta$ may be determined experimentally because it is specified by any of the relations (1.10.2e), (1.10.3g), (1.10.4f), and (1.10.5f) that involve well-defined properties of the system and surroundings, being differential forms appropriate to a QSI process. No restriction has been placed on the magnitude of the difference between intensive variables of the system and bath. In this sense, the present results represent a generalization of conventional irreversible thermodynamics, discussed in later sections.

Appendix A: Remarks Concerning Irreversible Processes

For a more transparent interpretation of irreversible processes, consider an entropy transfer from the reservoir to the system; the examination of the opposite case is left as an exercise. We rewrite Eq. (1.9.1c) in the form $dS(T, V, n_i) - |d_b S_0(T_0, V_0, n_{0i})| - \delta\theta = 0$, or as $dS(T, V, n_i) = |d_b S_0(T_0, V_0, n_{0i})| + \delta\theta$, with $T_0 > T$. This shows that the *total* entropy increase of the system (the left-hand side) consists of what is reversibly transferred out of the reservoir (recall the assumption that all reservoir processes are executed reversibly) plus what is irreversibly generated internally by the release of constraints. The latter events are beyond the control of the experimenter and are not transferred across the boundaries of the system. It is only when no such processes take place that the entropy increase in the system is matched by the corresponding entropy decrease in the surroundings at the common temperature T .

Correspondingly, as Eq. (1.10.2a) shows, the energy response to entropy changes involves the quantity $T_0(dS - \delta\theta)$. In conformity with the first law, it is only entropy transferred across the boundaries (with the internal contributions subtracted out from the total) that contributes to the energy of the system.

Appendix B: Time-Dependent Irreversible Processes

Here we show how to implement the irreversibility scheme by citing a specific example; see also Ref. 1. Consider a macroscopic system anchored to an enormous reservoir via a thin boundary layer, as depicted in Figure 1.10.1. Let T_0 , P_0 , and μ_0 be the intensive variables of the reservoir and let S_0 , V_0 , and n_0 be the relevant conjugate entropy, volume, and mole number. The corresponding quantities of the system lack the zero subscripts. The boundary, a thin layer of flexible material, permits the gradual exchange of heat and matter and allows for volume changes in the system and its surroundings. A typical temperature profile is shown in Figure 1.10.1: T and T_0 are essentially uniform over almost each of the two regions; the changeover occurs smoothly, but possibly precipitously, across the small boundary layer. Similar profiles obtain for the pressure and for the chemical potential. As is customary, the reservoir is assumed to be so huge that its intensive variables T_0 , P_0 , and n_0 remain constant, and that all processes within it take place reversibly.

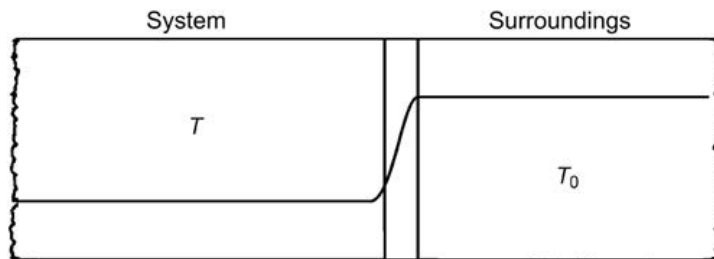


FIGURE 1.10.1

Temperature profile near the junction between a system (left) at temperature T and a reservoir (right) at temperature T_0 under QSI operating conditions. The change in temperature occurs over a narrow boundary region.

As a specific example, we introduce the Berthelot gas as the working substance; the equation of state is given by (a and b are materials-specific parameters)

$$P = \frac{nRT}{V - nb} - \frac{n^2a}{TV^2} \approx \frac{nRT}{V} \left(1 + \frac{nb}{V}\right) - \frac{n^2a}{TV^2}, \quad (1.10.10)$$

mandating the use of T , V , and n as the (independent) control variables. We assume QSIPs as operating conditions and base our further study on Eq. (1.10.3c) and on Eq. (1.10.3g):

$$T_0 d\theta = (T_0 - T) \left[(C_V/T) dT + (\partial P/\partial T)_{V,n} dV + \widehat{S} dn \right] - (P_0 - P) dV + (\mu_0 - \mu) dn, \quad (1.10.11)$$

To determine the entropy θ for a particular irreversible process, we specify T , V , and n as a function of time t and carry out the requisite integrations. Thus, we write

$$\begin{aligned} \theta = \int \left[\left(1 - \frac{T(t)}{T_0}\right) \right] & \left[\frac{C_{V,n}[T(t), V(t), n(t)]}{T(t)} \frac{dT}{dt} + \frac{\partial P}{\partial T} \frac{dV}{dt} + \widehat{S}(T(t), V(t)) \frac{dn}{dt} \right] dt \\ & - \int \frac{P_0}{T_0} \left(1 - \frac{P(t)}{P_0}\right) \frac{dV}{dt} dt + \int \frac{\mu_0}{T_0} \left(1 - \frac{\mu(t)}{\mu_0}\right) \frac{dn}{dt} dt, \end{aligned} \quad (1.10.12)$$

where the integral limits are taken between the initial time, $t_i = 0$, and the final time, $t_f = \tau$, as lower and upper limits, respectively.

Special Cases

For simplicity, we introduce several simplifications: (i) We restrict consideration to the case of fixed composition, which eliminates the third and fifth integrals in Eq. (1.10.12). (ii) For definiteness, we assume that the system is initially in a state with $T_i < T_0$ and $P_i < P_0$: T and P both increase when the interaction between the system and its surroundings is turned on. This requires, as a sufficient condition, that V for the system should diminish during the interaction; P adjusts in accordance with the adopted equation of state of the system. (iii) Correspondingly, V_0 for the reservoir increases so as to keep the volume of the compound unit fixed, as is required by the derivation leading to Eq. (1.10.2). (iv) During the interaction, the temperature of the system increases monotonically, from its initial value T_i to its final value $T_f < T_0$. The volume is manipulated to decrease from V_i to V_f such that at the end of the process, the prevailing pressure has increased from P_i to $P_f < P_0$.

We first attend to the specification of the entries in Eq. (1.10.12) as follows: introduce the caloric equation of state for the energy E and Eq. (1.10.10) to determine

$$\partial E/\partial V = T(\partial P/\partial T) - P = 2n^2a/V^2T \quad (1.10.13)$$

and integrate. The arbitrary function of temperature is set at $3nRT/2$, so that relative to an arbitrary reference value of the energy we obtain

$$E = 3nRT/2 - 2n^2a/VT; \quad C_{V,n} = (\partial E/\partial T)_{V,n} = 3nR/2 + 2n^2a/VT^2, \quad (1.10.14)$$

where $C_{V,n}$ is the heat capacity at constant volume and composition. Now substitute Eqs. (1.10.10) and (1.10.14) into Eq. (1.10.12). At constant composition, changes in temperature and volume of the system produce a change in entropy given by

$$\theta = \int \left(1 - \frac{T}{T_0}\right) \left[\frac{3nR}{2T} + \frac{2n^2a}{VT^3}\right] dT + \int \left\{ \left(\frac{nR}{V-nb} + \frac{n^2a}{V^2T^2}\right) - \frac{P_0}{T_0} - \frac{2}{T_0} \left(\frac{n^2a}{V^2T}\right) \right\} dV. \quad (1.10.15)$$

For ease of further handling, we split up the contributions into separate headings.

- (i) We first consider integrals that involve solely either T or V as the integration variable. These lead to ordinary integrals of the form:

$$\theta_0 = \frac{3nR}{2} \ln \frac{T_f}{T_i} - \frac{3nR}{2T_0} (T_f - T_i) - nR \ln \left[\frac{V_i - nb}{V_f - nb} \right] + \frac{P_0}{T_0} (V_i - V_f). \quad (1.10.16)$$

- (ii) For later use, we also study the entropy increase of the reservoir, whose volume increases reversibly from V_0 to $V_0 + (V_i - V_f)$ at fixed T_0, P_0 , which matches the volume change of the system. For this purpose, we adopt the fundamental relation $dS_0 = (1/T_0)(dE_0 + P_0 dV_0)$, with $dE_0 = (dE_0/dV_0)dV_0$ for fixed T_0 . On introducing Eqs. (1.10.10) and (1.10.13)—the reservoir is of the same composition as the system—and integrating, we find that the entropy change of the reservoir is given by

$$\begin{aligned} S_{0,f} - S_{0,i} &= \frac{2n_0^2a}{T_0^2} \left(\frac{1}{V_{0,i}} - \frac{1}{V_{0,f}} \right) + \frac{P_0}{T_0} (V_{0,f} - V_{0,i}) \approx \frac{2n_0^2a}{T_0^2} \left(\frac{V_i - V_f}{V_{0,i}^2} \right) + \frac{P_0}{T_0} (V_i - V_f) \\ &= \frac{2a}{T_0^2} c_0^2 (V_i - V_f) + \frac{P_0}{T_0} (V_i - V_f), \end{aligned} \quad (1.10.17)$$

where we had expanded the denominator for small values of $V_i - V_f$ relative to $V_{0,i}$; also, we set $c_0 \equiv n_0/V_0$ as the gas concentrations in the reservoir.

- (iii) Going back to the changes of the system, it remains to work with two types of line integrals in Eq. (1.10.15) that simultaneously involve both T and V in the integrand. The first deals with temperature changes that accompany heat transfers:

$$d\theta_T = \left(1 - \frac{T}{T_0}\right) \left[\frac{2n^2a}{VT^3}\right] dT, \quad (1.10.18)$$

and the second relates to volume changes that are produced by work exchange,

$$d\theta_V = \left\{ \frac{n^2a}{V^2T^2} - \frac{2}{T_0} \left(\frac{n^2a}{V^2T}\right) \right\} dV. \quad (1.10.19)$$

At this point, we must specify the time dependence for both T and V . We adopt two cases for further study:

Case 1. Let $V(t) = V_i e^{-k_V t}$, $T(t) = T_i e^{+k_T t}$, $0 \leq t \leq \tau$, where k_V and k_T are the time constants such that in the time interval $0 \leq t \leq \tau$, the volume (temperature) changes from the initial value V_i , (T_i) to the final value V_f , (T_f). Insert these two functions of time into Eq. (1.10.18) and set $dT = (dT/dt)dt$ to carry out the integrations which are perfectly straightforward but quite tedious. One finds that

$$\theta_T = + \frac{2n^2a}{V_i T_i} \left\{ \frac{1}{T_i(k_V/k_T - 2)} \left[\frac{V_i}{V_f} \left(\frac{T_i^2}{T_f^2} \right) - 1 \right] - \frac{1}{T_0(k_V/k_T - 1)} \left[\frac{V_i}{V_f} \left(\frac{T_i}{T_f} \right) - 1 \right] \right\}, \quad \frac{k_V}{k_T} = \frac{\ln(V_i/V_f)}{\ln(T_f/T_i)}. \quad (1.10.20)$$

Proceeding similarly with Eq. (1.10.19), using $dV = (dV/dt)dt$ one obtains

$$\theta_V = \frac{n^2a}{V_i T_i} \left\{ \frac{-1}{T_i(1 - 2k_T/k_V)} \left[\frac{V_i}{V_f} \frac{T_i^2}{T_f^2} - 1 \right] + \frac{2}{T_0(1 - k_T/k_V)} \left[\frac{V_i}{V_f} \frac{T_i}{T_f} - 1 \right] \right\}. \quad (1.10.21)$$

If the denominators such as $(k_V/k_T - 1)^{-1}$ or $(2k_T/k_V - 1)^{-1}$ approach zero, their multipliers in square brackets do likewise since under these conditions $V_f \rightarrow V_i$, $T_f \rightarrow T_i$; l'Hôpital's rule then shows that the respective products approach zero, as anticipated. Also, if in its final state, the system is equilibrated with its surroundings, then $T_f = T_0$; one also requires that V_f satisfies Eq. (1.10.10) with $P_f = P_0$.

Case 2: We consider the time dependence of the volume $V = V_i/(1 + k_V t)$, with the same temperature dependence as before. The upper limit for $k_V t$ is determined by the choice for the final volume, V_f . Equations (1.10.15)–(1.10.17) are the same as before. On substituting the assumed time dependence for temperature into Eq. (1.10.18), one obtains

$$\theta_T = + \frac{n^2a}{T_i^2 V_i} \left\{ \left[1 - \frac{T_i^2}{T_f^2} \right] + \frac{k_V}{2k_T} \left[1 - \frac{T_i^2}{T_f^2} + 2 \frac{T_i^2}{T_f^2} \ln \frac{T_i}{T_f} \right] \right\} - \frac{2n^2a}{T_i T_0 V_i} \left\{ \left[1 - \frac{T_i}{T_f} \right] + \frac{k_V}{k_T} \left[1 - \frac{T_i}{T_f} + \frac{T_i}{T_f} \ln \frac{T_i}{T_f} \right] \right\}, \quad \frac{k_V}{k_T} = \frac{V_i/V_f - 1}{\ln(T_f/T_i)}. \quad (1.10.22)$$

Proceeding similarly with Eq. (1.10.19), one finds that

$$\theta_V = \frac{n^2a}{V_i T_i} \frac{k_V}{k_T} \left\{ \frac{-1}{2T_i} \left(1 - \frac{T_i^2}{T_f^2} \right) + \frac{2}{T_0} \left(1 - \frac{T_i}{T_f} \right) \right\}. \quad (1.10.23)$$

Both these results clearly differ from Case 1.

Nevertheless, on eliminating the k_T/k_V ratios and summing Eqs. (1.10.20) and (1.10.21) or Eqs. (1.10.22) and (1.10.23), the *total* entropy change is exactly the same, namely:

$$\begin{aligned} \theta_V + \theta_T &= \frac{n^2a}{V_i T_i} \left\{ \frac{2}{T_0} \left[\frac{V_i T_i}{V_f T_f} - 1 \right] - \frac{1}{T_i} \left[\frac{V_i T_i^2}{V_f T_f^2} - 1 \right] \right\} \\ &= n^2a \left\{ \frac{2}{T_0} \left[\frac{1}{V_f T_f} - \frac{1}{V_i T_i} \right] - \left[\frac{1}{V_f T_f^2} - \frac{1}{V_i T_i^2} \right] \right\}. \end{aligned} \quad (1.10.24)$$

One may verify that precisely the same result is found on adopting other time-dependent changes for T and V . This should be considered a very general feature of the present strategy. One need hardly be

surprised. For, in going back to the very beginning, Eq. (1.9.1d), $d\theta$ is specified as a difference between two entropy terms, i.e., two functions of state.

The total entropy change of the compound system under the assumed conditions is the sum of Eqs. (1.10.16) and (1.10.24); the entropy change of the reservoir responding to the irreversible processes is given by Eq. (1.10.8).

For an ideal gas as a working substance $a = 0$, and Eqs. (1.10.15) and Eq. (1.10.16) are changed to

$$\theta_{ig} = \frac{3nR}{2} \ln \frac{T_f}{T_i} - \frac{3nR}{2T_0} (T_f - T_i) - nR \ln \left[\frac{V_i}{V_f} \right] + \frac{P_0}{T_0} (V_i - V_f). \quad (1.10.25)$$

Here the first and third terms agree with the entropy change accruing to the system under reversible operations.

Cyclic Processes

Also of interest is the execution of a circular process in which the initial state of the system is restored. To study this process, we attach to the system a second reservoir at temperature $T_1 < T_i$, pressure $P_1 < P_i$, that initially remains sealed off while the interaction between the system and the first reservoir proceeds as shown above. After the end point T_f and V_f has been reached, the first reservoir is sealed off and the interaction between the system and the second reservoir is initiated and maintained until the initial state of the system has been restored.

For the return path, the subscripts f and i in Eq. (1.10.16) must be interchanged and the subscript 0 must be replaced by 1. On adding this modified equation to Eq. (1.10.16) for the forward process, one obtains (in the approximation $nb \ll V$) the net contribution associated with (i) the path-independent integrals as

$$\theta_1 = \frac{3}{2} nR (T_f - T_i) \left(\frac{1}{T_1} - \frac{1}{T_0} \right) + R (V_i - V_f) [(c_0 - c_1) + (c_1^2 - c_0^2)b]. \quad (1.10.26)$$

We proceed similarly (ii) with the same index alterations to Eq. (1.10.17) to deal with the entropy contribution for the volume change of reservoir 1 in the reverse process. We also again expand P_1/T_1 and add the resultant to Eq. (1.10.19) to obtain

$$\theta_2 = a (V_i - V_f) \left(\frac{c_0^2}{T_0^2} - \frac{c_1^2}{T_1^2} \right) + R (V_i - V_f) [(c_0 - c_1) + (c_0^2 - c_1^2)b] \quad (1.10.27)$$

as the overall change in entropy of the two reservoirs. (iii) Last, we must evaluate the line integrals for the reverse process. Repeat the mathematical operations that led (for instance) to Case 1, but with $V(t) = V_i e^{+k_v t}$, $T(t) = T_i e^{-k_r t}$, $0 \leq t \leq \tau$. It turns out that we then recover Eq. (1.10.24) with the indices once more interchanged. When this resultant is added to Eq. (1.10.24), we obtain

$$\theta_3 = 2n^2 a \left[\frac{1}{V_f T_f} - \frac{1}{V_i T_i} \right] \left(\frac{1}{T_0} - \frac{1}{T_1} \right). \quad (1.10.28)$$

The total entropy change during the cyclic process is the sum of $\theta_1 + \theta_2 + \theta_3$.

The major contribution to the entropy changes in the cyclic process of the compound system is in the form

$$\theta = \frac{3}{2}nR(T_f - T_i) \left(\frac{1}{T_1} - \frac{1}{T_0} \right). \quad (1.10.29)$$

In fact, this is the sole contribution if an ideal gas ($a = b = 0$) is used as a working substance. In a strictly reversible process, the total entropy change would add up to zero. Remarkably, the major contribution, Eq. (1.10.29), is independent of the constitution of the gas phases, and depends only on the indicated temperatures.

The above example serves as a prototype on how to adapt the present methodology to other cases of interest, such as the use of different materials as working substances or the use of an alternative set of control variables.

Reference

1.10.1. J.M. Honig and Ross Hoehn, *Open J. Chem. Eng.* **5**, 1–6 (2011).

Notes

- 1.10.1.** A strictly logical presentation of the subject matter would have required me to terminate the derivations in the middle of each subsection (Eqs. (1.10.3e), (1.10.4d) and (1.10.5d)), until the material of Section 1.12 was presented, and then resuming the remaining material in the present section. It seemed pedagogically more attractive to preserve the continuity of the present exposition by citing material that will be proved in Section 1.12. You should convince yourself that this does not involve circular reasoning but a mere rearrangement of independent derivations.
- 1.10.2.** This condition is actually too restrictive. We need merely demand that any change in volume of the system be exactly matched by a corresponding compensating change in the volume of the surroundings. The latter may also be subject to other volume changes not related to the process under study.
- 1.10.3.** Again, what is meant here is a process in which an intensive variable Z of the system approaches Z_0 for the surroundings in the limit $(Z - Z_0) \rightarrow 0$.
- 1.10.4.** Alert readers may question why we may use substitutions for partial entropy derivatives that, as shown later, apply only to reversible processes. This step is permissible since S is a function of state whose characteristics may be specified by a study of the same process executed reversibly. The irreversibilities are handled through the $\delta\theta$ term.
- 1.10.5.** See for example: Ross Hoehn and J.M. Honig, *Acta Phys. Polon. A* **119**, 279–283 (2011). J. M. Honig and Ross Hoehn, *Open J. Chem. Eng.* **5**, 1–6 (2011). E. Duselis and J.M. Honig, *Eur. Chem. Bull. A* **1**, 175–180 (2012).
- 1.10.6.** A reminder: in light of Appendix A or the discussions of Eqs. (1.9.3e) and (1.10.2f), Eq. (1.9.1d) may be rewritten in the form $d_b S = -(dS - \delta\theta)$, which shows that the entropy exchanged between the system and the reservoir does include the portion generated irreversibly within the system.

1.11 Statements of the Second Law; Thermodynamic Operation of Heat Engines; Kelvin and Planck Statements; Temperature Scale

Operation of Heat Engines

Here is an early application of thermodynamic principles, which is simultaneously an illustration of irreversible processes: consider the operation of a heat engine attached to two very large thermal reservoirs: a hot unit set at temperature T_0^h and a cold stage maintained at temperature T_0^c . We wish to determine the efficiency at which the engine operates. To be useful as a continuous source of power, the engine must be capable of working in cycles; at the completion of every one of these, the engine returns to its starting point. All net changes accompanying the operation of the engine thus occur in the universe—another illustration of the importance of taking events in surroundings into account.

The operating reservoirs again are assumed so large that heat transfers do not appreciably alter the temperatures of each. Let Q_h be the heat transfer per cycle across the boundary between the hot reservoir and the engine ($Q_h > 0$ or $Q_h < 0$ accordingly as heat flows into or is rejected by the engine at the hot junction), and let Q_c be the heat transfer per cycle across the boundary separating the engine and the cold reservoir ($Q_c > 0$ or $Q_c < 0$ accordingly as heat is caused to flow into or is rejected by the engine at the cold junction).

In the operation of the engine, let $Q_h > |Q_c|$, or $Q_h - |Q_c| > 0$, so that, in conformity with the first law, this imbalance is reflected as work performed *by* the engine (the system) during each cycle *on* surroundings with which it interacts via a separate interface. Thus, work W performed *on* the engine is negative: $W < 0$. The efficiency for this energy conversion per cycle is specified by the defining relation

$$\eta \equiv \text{Work out/Heat in.} \quad (1.11.1)$$

To evaluate this quantity, recall that in each cyclic process, no matter how executed, the total entropy change *for the engine* is zero; thus, in view of Eq. (1.9.3e),

$$\oint dS = \oint (\delta Q/T_0 + \delta \theta) = 0 \quad \text{or} \quad \oint \delta_i Q/T_0 = -\oint \delta \theta < 0. \quad (1.11.2)$$

In the present case, the cyclic process degenerates into the Clausius sum

$$\frac{Q_h}{T_0^h} - \frac{\bar{Q}_c}{T_0^c} \leq 0, \quad (1.11.3)$$

where we introduced $\bar{Q}_c \equiv -Q_c > 0$ as a positive quantity. The equality in Eq. (1.11.3) holds when the engine operates reversibly. Equation (1.11.3) may be rewritten as

$$Q_h/T_0^h \leq \bar{Q}_c/T_0^c \quad \text{or} \quad \bar{Q}_c/Q_h \geq T_0^c/T_0^h \quad \text{or} \quad -\bar{Q}_c/Q_h \leq -T_0^c/T_0^h. \quad (1.11.4)$$

$$\eta = \frac{W}{Q_h} = \frac{Q_h - \bar{Q}_c}{Q_h} = 1 - \frac{\bar{Q}_c}{Q_h} \leq 1 - \frac{T_0^c}{T_0^h} \equiv \eta_{\text{Carnot}}. \quad (1.11.5)$$

This imposes an upper bound on the possible efficiency of the heat engine. Note the following points:

- (i) The temperatures involved are those of the heat reservoirs, not those of the engine parts in contact with the external sources; the two will necessarily differ in irreversible heat transfers prevailing under actual operations.
- (ii) No reference has been made to specific processes other than the restriction to cyclic events and to engines operating while in contact with two reservoirs of immense size. Thus, the above results obtain no matter what material is used as the actual working substance.
- (iii) The efficiency relates to the heat transfer across the hot junction.
- (iv) The equality sign applies only to reversible processes; the efficiency for any irreversible process is always less than that for a reversible one.
- (v) Even a reversible process can never be 100% efficient since the limiting values $T_0^c \rightarrow 0$ or $T_0^h \rightarrow \infty$ are inaccessible (Section 1.13). The efficiency becomes greater the larger T_0^h/T_0^c is.

Statements (i) and (iv) are sometimes called the *first and second theorems of Carnot*.

The Carnot Engine as a Heat Pump

If the above engine is run backward, one deals with a refrigerator or heat pump: by performance of work, heat is extracted from the cold junction and delivered to the hot reservoir. Here it is sensible to introduce the figure of merit or ideal heating efficiency as $Q_h/W = T_0^h/T_0^h - T_0^c$, the inverse of the Carnot efficiency derived above. The above ratio is rendered larger, the smaller the temperature difference between the hot and cold reservoir. See also Query 1, below.

Kelvin and Planck Statements of the Second Law

We are now in a position to recast the second law in a manner frequently adopted in elementary introductions to the second law. Statement (v) above provides the basis for *Kelvin's formulation of the second law*:

It is impossible to devise an engine which, working in cycles, shall produce no effect other than to extract heat from a reservoir and to perform an equal amount of work.

By working the derivations given here and in earlier sections in reverse, we can see that this statement implies the validity of the second law.

Related to the above is the Clausius statement of the second law:

It is impossible to devise a machine which, operating in cycles, transfers heat from a colder to a hotter body without producing any other effects in the universe.

This may be demonstrated by noting what would happen if the Clausius statement were incorrect. If no other changes occurred in the universe, then the heat extracted from the cold reservoir must be transferred without loss to the heat reservoir. Equation (1.11.4) would then read $-\bar{Q}_h/T_0^h + Q_c/T_0^c \leq 0$, together with the requirement that $Q_h = |Q|_c$. This implies that $T_0^h/T_0^c \leq 1$, which is a contradiction of terms.

Thermodynamic Temperature Scale

Carnot efficiency measurements, executed reversibly, furnish a means of measuring temperatures, regardless of the nature of working substances: for, Eq. (1.11.5) contains no reference to any working

material. This calibration might be achieved by equilibrating one of the engine interfaces with a large body of a standard, such as water at its triple point of water, set at 273.16 K on the gas temperature scale. The second interface is connected to a large body whose temperature is to be established. By adjusting conditions so that the engine operates reversibly while maintaining contact with the two external bodies, and measuring the concomitant heat and work transfers (in the idealization contemplated here this entails no problems!). The efficiency of operation then determines the unknown temperature of the body. A detailed discussion is provided in Section 2.4, where we relate the cycling of the Carnot engine to a comparable thermal cycling of an ideal gas. This directly establishes the identity between the two temperature scales.

Incidentally, the fact that for a reversible cyclic process, the sum

$$\left[\frac{Q_h}{T_0^h} - \frac{\bar{Q}_c}{T_0^c} \right]_{rev} = 0 \quad (1.11.6)$$

vanishes verifies that the ratio Q/T represents a function of state which we have previously identified as the entropy.

Exercise

- 1.11.1.** Examine more closely the case of a working refrigerator, in which, by carrying out work on the engine, heat is withdrawn from the cold reservoir and discharged at the hot reservoir.

1.12 Systematization of Results Based on Functions of State

Back to fundamentals! This is going to be a long section. By now, we have set up useful functions of state for processes involving the transfer of heat, performance of mechanical work, and movement of chemical species across the boundaries of a system. We now initiate a standard, systematic investigation that shows how these functions of state can be used to characterize reversible processes. This produces a whole cornucopia of useful relationships. Again, these functions depend solely on the difference between initial and final equilibrium states; we thus dispense with quantities such as heat and work that are individually path dependent.

Let us begin by restating in differential form the four functions of state for reversible processes developed earlier. Starting with the differential for the *energy*,

$$dE = TdS - PdV + \sum_i \mu_i dn_i, \quad (1.12.1a)$$

we introduce the definition $H = E + PV$ in differential form $dH = dE + PdV + VdP$ to find the differential form for the *enthalpy*

$$dH = TdS + VdP + \sum_i \mu_i dn_i. \quad (1.12.1b)$$

Proceeding similarly with the definition for the *Helmholtz (free) energy*

$$A = E - TS, \quad dA = dE - TdS - SdT, \quad \text{we find that}$$

$$dA = -SdT - PdV + \sum_i \mu_i dn_i. \quad (1.12.1c)$$

Lastly, setting $G = E + PV - TS$, we obtain for differential form for the *Gibbs (free) energy* as

$$dG = -SdT + VdP + \sum_i \mu_i dn_i. \quad (1.12.1d)$$

The process of proceeding as above from one state function to the next by interchange of independent variables is known as executing *Legendre transformations*. Thus, no one function is in any sense more fundamental than any other.

Clearly, the choice of the functions E , H , A , or G is governed by the experimental conditions. For example, when temperature and pressure are under experimental control, one chooses the Gibbs free energy as the appropriate function of state from which to make further deductions. Processes carried out under adiabatic and constant pressure conditions are to be characterized by the enthalpy state function. We now show how the above functions of state may be determined experimentally, and how to choose the appropriate one with which to work under the selected operating conditions.

Thermodynamic Interrelations; Maxwell Equations, and Equations of State

At this point, the systematics kicks in. An enormous amount of useful information may be generated by a systematic application of elementary steps, thereby illustrating the power of thermodynamic methodology.

(a) We begin by taking first derivatives of the above state functions E , H , A , and G with respect to the appropriate independent variables S , T , P , V , and n_i . This leads to the Table 1.12.I:

The above is all well and dandy; the math is fine, but what good are these relations? As an answer, we introduce the *equation of state* for any material: it provides interrelations among experimental variables in the form

$$V = V(T, P, n_i) \text{ or } P = P(T, V, n_i). \quad (1.12.2a)$$

Table 1.12.I Listing of First Derivatives of Thermodynamic Functions of State

[1]	$T = (\partial E / \partial S)_{V, n_i} = (\partial H / \partial S)_{P, n_i}$
[2]	$S = -(\partial A / \partial T)_{V, n_i} = -(\partial G / \partial T)_{P, n_i}$
[3]	$V = (\partial H / \partial P)_{S, n_i} = (\partial G / \partial P)_{T, n_i}$
[4]	$P = -(\partial E / \partial V)_{S, n_i} = -(\partial A / \partial V)_{T, n_i}$
[5]	$\mu_i = (\partial E / \partial n_i)_{S, V, n_{j \neq i}} = (\partial H / \partial n_i)_{S, P, n_{j \neq i}} = (\partial A / \partial n_i)_{T, V, n_{j \neq i}} = (\partial G / \partial n_i)_{T, P, n_{j \neq i}}$
[6]	$\mu_i = -T(\partial S / \partial n_i)_{E, V, n_{j \neq i}} = -T(\partial S / \partial n_i)_{H, P, n_{j \neq i}}$

When these relations are used in [3], for example, an integration with respect to P yields $H(T,P,n_i)$ under adiabatic conditions at constant composition (remember, these relations hold only for reversible processes!) or yields $G(T,P,n_i)$ under isothermal conditions at constant composition. Similarly, use of Eq. (1.12.2a) in [4], followed by an integration with respect to V specifies E and A , respectively, under adiabatic and isothermal conditions at constant composition. Conversely, determining the pressure via relation [4] is useful when direct measurements (e.g., the pressure exerted by electrons in a metal) are difficult; methods of specifying A or E will be introduced in due time—be patient. Further, once A or G are known—and methods other than those just cited will be introduced later—the differentiations called for in [2] will yield the entropy $S(T,V,n_i)$ or $S(T,P,n_i)$.

We come now to relations [5] and [6]. The question to be settled first is whether all the listed chemical potentials are in fact identical, or whether they should be regarded as six distinct quantities. In an appendix to this section, they are shown to be identical. If the various functions of state have been determined by the above procedure, or by methods described later, then the chemical potential, which governs the transfer of matter, can be found by differentiation. Actually, sets [5] and [6] are frequently employed in reverse: for example, the chemical potential may be determined by various electrochemical measurements, as shown in Chapter 4; integration with respect to the relevant mole number n_i then yields the desired thermodynamic function of state. Care has to be exercised that the experimental conditions prescribed by the subscripted variables are in fact held fixed.

- (b) As a second step, let us now execute a cross-double differentiation on each of the various functions of state in either order. As an example, consider the operation $(\partial^2 E / \partial S \partial V)_{n_i} = (\partial^2 E / \partial V \partial S)_{n_i}$ on the energy function, using Eq. (1.12.1a). This directly yields $(\partial T / \partial V)_{S,n_i} = -(\partial P / \partial S)_{V,n_i}$. A compilation resulting from this type of operations on Eqs. (1.12.1b)–(1.12.1d) is provided in Table 1.12.II.

The above 12 relations are known as *Maxwell equations*. Again, the question arises: what good are they? Here, Eqs. [7] and [8] are particularly useful because entropy meters are not available: so, Eqs. [7] and [8] are used to eliminate the unknown partial derivatives of entropy with respect to pressure or

Table 1.12.II Table of Maxwell Relations, Based on Thermodynamic Functions of State

[1]	$(\partial T / \partial V)_{S,n_i} = -(\partial P / \partial S)_{V,n_i}$
[2]	$(\partial T / \partial P)_{S,n_i} = (\partial V / \partial S)_{P,n_i}$
[3]	$(\partial T / \partial n_i)_{S,V,n_{j \neq i}} = (\partial \mu_i / \partial S)_{V,n_i}$
[4]	$(\partial T / \partial n_i)_{S,P,n_{j \neq i}} = (\partial \mu_i / \partial S)_{P,n_i}$
[5]	$(\partial V / \partial n_i)_{T,P,n_{j \neq i}} = (\partial \mu_i / \partial P)_{T,n_i}$
[6]	$(\partial V / \partial n_i)_{S,P,n_{j \neq i}} = (\partial \mu_i / \partial P)_{S,n_i}$
[7]	$(\partial S / \partial P)_{T,n_i} = -(\partial V / \partial T)_{P,n_i}$
[8]	$(\partial S / \partial V)_{T,n_i} = (\partial P / \partial T)_{V,n_i}$
[9]	$(\partial S / \partial n_i)_{T,V,n_{j \neq i}} = -(\partial \mu_i / \partial T)_{V,n_i}$
[10]	$(\partial S / \partial n_i)_{T,P,n_{j \neq i}} = -(\partial \mu_i / \partial T)_{P,n_i}$
[11]	$(\partial P / \partial n_i)_{T,V,n_{j \neq i}} = -(\partial \mu_i / \partial V)_{T,n_i}$
[12]	$(\partial P / \partial n_i)_{S,V,n_{j \neq i}} = -(\partial \mu_i / \partial V)_{S,n_i}$

volume—which raise their ugly heads in many of our subsequent operations—in favor of the known partial derivatives of the equation of state. This also addresses the awkward situation of Eqs. (1.12.1), where the two state functions E and H are expressed in terms of another state function, S . The actual procedure will be illustrated shortly. It should be obvious how [5], [6] or [11], [12], coupled with the equation of state, may be employed to determine the chemical potential under a variety of different experimental conditions. Knowledge of this quantity will come in handy later on. Further, [9] and [10] provide a route to determine the differential entropy or to eliminate these quantities if the chemical potential is known in its dependence on T at constant P or on V and at constant composition.

(c) Let us look next at the differentiation of the extensive quantities with respect to composition variables, in which all intensive variables are held fixed. Relations [5] and [10], involving the fixed intensive variables T and P , namely

$$\begin{aligned}\bar{V} &\equiv (\partial V / \partial n_i)_{T,P,n_{j \neq i}} = (\partial \mu_i / \partial P)_{T,n_i}; \\ \bar{S} &\equiv (\partial S / \partial n_i)_{T,P,n_{j \neq i}} = -(\partial \mu_i / \partial T)_{P,n_i}\end{aligned}\tag{1.12.2b}$$

and the functions

$$\mu_i = (\partial G / \partial n_i)_{T,P,n_{j \neq i}} \equiv G, \quad \bar{H}_i \equiv (\partial H / \partial n_i)_{T,P,n_{j \neq i}},\tag{1.12.3}$$

are of special interest; these are known as *partial molal quantities*. Similar derivatives, such as [6] or [9], for which at least some extensive quantities (other than the n_i) are held constant, are known as *differential forms*. Also, from $G = H - TS$, we deduce that

$$\mu_i = \bar{H}_i - T\bar{S}_i.\tag{1.12.4}$$

In succeeding sections and chapters, we encounter methods for the experimental determination and utilization of the above functions.

Intervening Comments

Equation (1.12.1a) deserves careful scrutiny. As is shown by the entries in Tables 1.12.I and 1.12.II, the entropy depends not only on T but also on variables such as V , P , and n_i , and other quantities that are cited in Chapter 5. Thus, it is the totality of these functions—not just the heat transfer which was used in introducing S as a function of state—that must be taken into consideration in determining the entropy function.

Caloric Equations of State

So far we have set up the energy and enthalpy in differential form, where $E = E(S,V,n_i)$ and $H = H(S,P,n_i)$ are specified in terms of the indicated independent variables. These particular functions are said to involve *natural coordinates*. However, as already stated, the differentials of E and H are set up in terms of another function of state, the entropy S , which makes it unclear how we are to proceed further. As a remedy, we express the entropy in its terms of its dependence on temperature, volume or pressure, and composition either as $S = S(T,V,n_i)$ or as $S = S(T,P,n_i)$. We then introduce the differential form (1.3.19) for dS , whereby the first law may be recast in the form

$$dE = T \left[(\partial S / \partial T)_{V, n_i} dT + (\partial S / \partial V)_{T, n_i} dV + \sum_i (\partial S / \partial n_i)_{T, V, n_{j \neq i}} dn_i \right] - PdV + \sum_i \mu_i dn_i. \quad (1.12.5)$$

The energy has now been expressed in terms of *unnatural coordinates*, namely T , V , and n_i . The above expression correlates with the following differential analytic form for the energy $E = E(T, V, n_i)$:

$$dE = (\partial E / \partial T)_{V, n_i} dT + (\partial E / \partial V)_{T, n_i} dV + \sum_i (\partial E / \partial n_i)_{T, V, n_{j \neq i}} dn_i. \quad (1.12.6)$$

On matching coefficients, we obtain the following relations:

$$(\partial E / \partial T)_{V, n_i} = (\partial S / \partial T)_{V, n_i} \equiv C_V \quad (1.12.7a)$$

$$(\partial E / \partial V)_{T, n_i} = T(\partial P / \partial T)_{V, n_i} - P \quad (1.12.7b)$$

$$(\partial E / \partial n_i)_{T, V, n_{j \neq i}} \equiv \hat{E}_i. \quad (1.12.7c)$$

These relations are immediately useful. In Eq. (1.12.7a), we have introduced C_V as the *heat capacity at constant volume*, a quantity that can be experimentally determined in its dependence on temperature, as shown in Section 1.15. Thus, via the integrations $E - E_0 = \int C_V dT$ or $S - S_0 = \int (C_V / T) dT$, one finds directly the variation of energy or entropy with temperature when the volume and composition of the system are held constant.

Equation (1.12.7b) is the so-called *caloric equation of state*, into which we had introduced the appropriate Maxwell relation [8] of Table 1.12.II. Thus, if the equation of state $P = P(T, V, n_i)$ is known for a given system, then its energy at a given temperature and composition is found by integration with respect to V . This provides a second method for finding the energy function of a system.

Equation (1.12.7c) simply introduces a short-hand symbol for the indicated differential form. Once $E(T, V, n)$ has been obtained as just described, Eq. (1.12.7b) is found by differentiation with respect to mole number.

In summary, the energy differential in unnatural coordinates may be written out as

$$dE = C_{V, n_i} dT + \left[T(\partial P / \partial T)_{V, n_i} - P \right] dV + \sum_i \hat{E}_i dn_i. \quad (1.12.8)$$

Corresponding arguments hold for the enthalpy; here one works with the entropy function $S = S(T, P, n_i)$, relation [7] of Table 1.12.II, and the differential forms

$$\begin{aligned} dH &= T \left[(\partial S / \partial T)_{P, n_i} dT + (\partial S / \partial P)_{T, n_i} dP + \sum_i (\partial S / \partial n_i)_{T, P, n_{j \neq i}} dn_i \right] + VdP + \sum_i \mu_i dn_i \\ &= (\partial H / \partial T)_{P, n_i} dT + (\partial H / \partial P)_{T, n_i} dP + \sum_i (\partial H / \partial n_i)_{T, P, n_{j \neq i}} dn_i. \end{aligned} \quad (1.12.9)$$

On matching coefficients, one obtains

$$(\partial H / \partial T)_{P, n_i} = T(\partial S / \partial T)_{P, n_i} = C_P \quad (1.12.10a)$$

as the expression for the *heat capacity at constant pressure* and composition; this quantity can be found experimentally as a function of T . Integration with respect to temperature then yields the

enthalpy or entropy if the variation of the heat capacity with temperature and composition is known from experiment or theory. Moreover, using Eq. [7] of Table 1.12.II,

$$(\partial H/\partial P)_{T,n_i} = -T(\partial V/\partial T)_{P,n_i} + V \quad (1.12.10b)$$

is found to be the appropriate caloric equation; integration of the right-hand side, involving $V(T,P,n_i)$, with respect to P provides a means to establish the enthalpy. Finally,

$$\bar{H}_i \equiv (\partial H/\partial n_i)_{T,P,n_{j \neq i}} \quad (1.12.10c)$$

is the relevant partial molal variable. The differential of the enthalpy in *unnatural coordinates* reads

$$dH = C_{P,n_i}dT + \left[-T(\partial V/\partial T)_{P,n_i} + V \right]dP + \sum_i \bar{H}_i dn_i. \quad (1.12.11)$$

We may replace $(\partial V/\partial T)_{P,n_i}$ with αV , where α is the isobaric coefficient of thermal expansion. So, we have found a second route for determining the enthalpy: carry out the integrations called for in Eq. (1.12.11).

Two Important Relations

Two relations will be extensively used in later derivations: according to Table 1.12.II, entry [5], we write

$$(\partial \mu_i/\partial P)_{T,n_{j \neq i}} = \bar{V}_i \equiv (\partial V/\partial n_i)_{T,n_{j \neq i}}. \quad (1.12.12)$$

Also, starting with $G/T = H/T - S$, we obtain

$$d(G/T) = -(H/T^2)dT + dH/T - dS = -(H/T^2)dT + VdP/T. \quad (1.12.13)$$

Thus, at constant P and composition,

$$\left[\frac{\partial(G/T)}{\partial T} \right]_{P,n_i} = -\frac{H}{T^2}. \quad (1.12.14a)$$

Since G and H depend on the $\{n_i\}$, we may first take partial derivatives of Eq. (1.12.14a) with respect to n_i at constant T and P . Then, on interchanging the order of differentiation on the left-hand side, we obtain

$$\left[\frac{\partial(\mu_i/T)}{\partial T} \right]_{P,n_{j \neq i}} = -\frac{\bar{H}_i}{T^2}, \quad (1.12.14b)$$

a relation that will be cited frequently in our further development.

Lastly, insertion of Eq. [2] of Table 1.12.I into $A = E - TS$ leads to

$$A = E + T(\partial A/\partial T)_{V,n_i}; (\partial A/\partial T)_{V,n_i} = (A - E)/T; E = A - T(\partial A/\partial T)_{V,n_i}. \quad (1.12.15)$$

Similarly, one finds

$$G = H + T(\partial G/\partial T)_{P,n_i}; (\partial G/\partial T)_{P,n_i} = (G - H)/T; H = G - T(\partial G/\partial T)_{P,n_i}. \quad (1.12.16)$$

The above relations are known as *Gibbs–Helmholtz equations*. The solution of these partial differential equations, as indicated in Eq. (1.3.27), and after insertion for E or H from the integrated version of Eqs. (1.12.8) and (1.12.11), yields $A = A(T, V, n_i)$ or $G = G(T, P, n_i)$. Note how the right-hand sides furnish methods to determine E or H complementary to Eqs. (1.12.7b) and (1.12.10b). We have thus achieved a complete specification of the various thermodynamic functions of interest in terms of experimental information. We shall later cite several other experimental techniques for determining these quantities.

Determination of Functions of State

So far so good, but how do we execute some of the above steps in practice? By way of illustration, consider a nonideal gas of constant composition. Since energy occupies such an important role, let us use Eq. (1.12.8) as a starting point and integrate between initial conditions (T_1, V_1) and final conditions (T_2, V_2) to obtain

$$E(T_2, V_2) = E(T_1, V_1) + \int_{T_1}^{T_2} C_V(T, V_1) dT + \int_{V_1}^{V_2} [T_2(\partial P/\partial T) - P] dV. \quad (1.12.17a)$$

As written, the first term on the right can serve as a reference or standard energy that is completely arbitrary, and thus may be chosen as is most convenient for the case under study. Indicate this choice for temperature and volume by an asterisk T^* and V^* ; these parameters will be held fixed during our study. Let us then eliminate all subscripts in Eq. (1.12.17a). We write for any value of T and V of interest

$$E(T, V) = (T^*, V^*) + \int_{T^*}^T C_V(T, V^*) dT + \int_{V^*}^V [T(\partial P/\partial T) - P] dV. \quad (1.12.17b)$$

Then, knowing the equation of state, $P = P(T, V)$, and the (empirical or theoretical) dependence of the heat capacity on temperature, we may integrate the right-hand side to obtain E relative to the chosen standard state at the temperature and volume of interest. How this is done for two specific cases is shown in the appendix.

Let us also consider the special case $T = T^*$, which eliminates the first integral in Eq. (1.12.17b), and, as is often done, refer the energy of the real gas to that of the *ideal gas* at that same temperature. The reference state thus does not involve V . We then set $E(T^*) = (3/2)nRT^*$, as the law of equipartition of energy for an ideal gas in statistical mechanics dictates. Then, the lower limit on the second integral in Eq. (1.12.17b) must be consistent with the volume of the ideal gas. To ensure the absence of any interactions in that regime the reference volume V^* must approach infinity. Thus, for the actual gas of interest Eq. (1.12.17b) reduces to

$$E(T, V) = (3/2)nRT + \lim_{v \rightarrow \infty} \int_v^V \left[T \left(\frac{\partial P}{\partial T} \right) - P \right] dV. \quad (1.12.18)$$

This specifies the energy of nonideal gases at temperature T and volume V relative to that of the ideal gas at temperature T . Commonly used equations of state may be approximated such that the integrands in Eq. (1.12.18) are of the form $1/V^q$, with $q \geq 2$; hence the lower limit occasions no difficulty.

The enthalpy of the nonideal gas is obtained by adding to the above its equation of state $P = P(T, V)$, multiplied by V .

Alternatively, the specification of the enthalpy proceeds similarly. Assuming constant composition we set

$$H(T_2, P_2) = H(T_1, P_1) + \int_{T_1}^{T_2} C_P(T, P_1) dT + \int_{P_1}^{P_2} [V - T_2(\partial V / \partial T)_P] dP. \quad (1.12.19a)$$

Here the enthalpy of the substance is referred to that of a reference standard for that material chosen at any convenient reference temperature T_1 and pressure P_1 . This formulation is particularly useful for condensed phases. In the approximation of Dulong and Petit, the reference value for *atomic solids* at sufficiently high temperatures is approximated by $3nR$. The partial derivative for volume in the integrand may be replaced by αV , where α is the isobaric coefficient of thermal expansion, which is fairly insensitive to pressure changes. For such materials, we cast the above in the form

$$H(T, P) = H(T^*, P^*) + \int_{T^*}^T C_P(T, P^*) dT + \int_{P^*}^P [V - T\alpha V] dP. \quad (1.12.19b)$$

The procedure is illustrated in more detail in the appendix.

To determine the entropy, we expand $S = S(T, V, n_i)$ as shown in the first term of Eq. (1.12.5) and introduce entry [7] and [8] of Table 1.12.II, Eq. (1.12.7a), and set $\hat{S} \equiv (\partial S / \partial n_i)_{T, V, n_{j \neq i}}$ to write

$$S(T_2, V_2, n_2) = S(T_1, V_1, n_1) + \int_{T_1}^{T_2} \frac{C_V(T, V_1, n_1)}{T} dT + \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T} \right)_{V, n_i} dV + \sum_i \int_{n_1}^{n_2} \hat{S}_i dn_i. \quad (1.12.20a)$$

Then, on regarding the first term on the right as a reference standard and eliminating subscripts, we obtain

$$S(T, V, n) = S(T^*, V^*, n^*) + \int_{T^*}^T \frac{C_V(T, V^*, n^*)}{T} dT + \int_{V^*}^V \left(\frac{\partial P}{\partial T} \right)_{V, n_i} dV + \sum_i \int_{n_i^*}^{n_i} \hat{S}_i dn_i. \quad (1.12.20b)$$

In the same vein, we utilize the expansion of $S = S(T, P, n_i)$ as shown in Eq. (1.12.9), coupled with entry [7] in Table 1.12.II, and Eq. (1.12.10a) to write

$$S(T, P, n) = S(T^*, P^*, n^*) + \int_{T^*}^T \frac{C_P(T, P^*, n^*)}{T} dT - \int_{P^*}^P \left(\frac{\partial V}{\partial T} \right)_{P, n_i} dP + \sum_i \int_{n_i^*}^{n_i} \bar{S}_i dn_i. \quad (1.12.20c)$$

For gases, it is conventional to select the ideal gas at a standard pressure of 1 bar as the reference standard.

As already mentioned, in the appendix, we illustrate by examples how the above relations are utilized. There is more to the application of these relations than meets the eye.

Equilibrium State Reviewed

We have seen earlier that after processes have run their course, the various functions of state E , H , A , G , and $-S$ have assumed minimal values consistent with the constraints imposed on the system. To undo the minimization state, work must be executed, or, as a special case, material must be transferred across the boundaries of the system. On this basis, we may reiterate earlier statements by identifying *the equilibrium state as that for which the appropriate thermodynamic function of state* (depending on the various applicable constraints) *is at a minimum*, except for entropy, which is at a maximum. Again, any displacement from this state requires a relaxation of the constraints and/or performance of work and/or transfer of matter across boundaries. We later indicate how functions of state may be found via caloric equations.

Clarification Concerning the Concept of Heat

We are now in a position to take up once more the thorny issue of what constitutes “heat”. While it is difficult to provide a tidy division between heat and work, it seems reasonable to base the discussion on the evolution of the entropy during any given process. In a system subject to heat transfer, the performance of mechanical work, and transfer of matter across its boundaries, the entropy is a function of T , V , and n_i . Correspondingly, we distinguish between three different contributions to the entropy: (a) $(\partial S/\partial n_i)dn_i$ —the (infinitesimal) entropy change arising from the transfer of matter across the boundaries of the system; (Note that this does not include changes in properties taking place locally within the system—more on that later.) (b) $(\partial S/\partial V)dV$ —which covers the volume change due to the performance of work on or by the system; (c) $(\partial S/\partial T)dT$ —the remaining entropy change, which must then be associated with the heat flow into or out of the system. This corresponds to the first mantra: “Anything that is not work is heat”.

As an aside, heating does not necessarily result in an increase of the temperature of the body. A counterexample is furnished by a reversible phase change, such as the melting of ice. Leaving aside concomitant volume and compositional alterations, any such phase changes arise from heating or cooling and should be considered as falling into category (c).

We must finally consider the effect of entropy changes from processes that take place entirely within a system. To avoid pitfalls we recognize that such events are outside the control of an experimentalist. By definition, then, no matter how slowly these changes might occur, they evolve irreversibly; the initial state cannot be restored without external interventions that incur other changes in the universe. Thus we must invoke Section 1.10, where such contributions to the entropy of the system are symbolized by $d\theta$. This quantity must then be added to the entropy changes (a)–(c) listed previously. However, the energy change dE is specified by Eq. (1.10.2a), which varies as $T_0(dS - d\theta)$, that is, it incurs only the entropy change in which the purely internal contribution has been subtracted out. This thus provides the second mantra: “Any purely internal rearrangements do not change the energy.” For further discussion see also Section 1.16.

Appendix: Uniqueness of the Chemical Potential

We demonstrate the uniqueness of the chemical potential by considering two particular cases; at constant temperature,

$$\mu_i = (\partial A / \partial n_i)_{T,V,n_{j \neq i}} - T(\partial S / \partial n_i)_{T,V,n_{j \neq i}}. \quad (1.12.21)$$

Now use Eq. (1.3.6) with $x \rightarrow n_i, v \rightarrow T, V, n_{j \neq i}, y \rightarrow S, V, n_{j \neq i}$, to write

$$(\partial E / \partial n_i)_{T,V,n_{j \neq i}} = (\partial E / \partial n_i)_{S,V,n_{j \neq i}} + (\partial E / \partial S)_{V,n_i} (\partial S / \partial n_i)_{T,V,n_{j \neq i}}. \quad (1.12.22)$$

With $(\partial E / \partial S)_{T,V,n_{j \neq i}} = T$, we find that

$$(\partial A / \partial n_i)_{T,V,n_{j \neq i}} = (\partial E / \partial n_i)_{S,V,n_{j \neq i}} = \mu_i, \quad (1.12.23)$$

showing that the chemical potential for the state function E is the same as for the state function A so long as the various constraining conditions are properly attended to.

Similarly, starting with the defining relation Eq. (1.12.3), we write

$$\mu_i = (\partial G / \partial n_i)_{T,P,n_{j \neq i}} = (\partial A / \partial n_i)_{T,P,n_{j \neq i}} + P(\partial V / \partial n_i)_{T,V,n_{j \neq i}}, \quad (1.12.24)$$

and we again introduce Eq. (1.3.6) in the first term on the right to write

$$\mu_i = (\partial A / \partial n_i)_{T,V,n_{j \neq i}} + (\partial A / \partial V)_{T,n_i} (\partial V / \partial n_i)_{T,P,n_{j \neq i}} + P(\partial V / \partial n_i)_{T,P,n_{j \neq i}}. \quad (1.12.25)$$

However, on account of Eq. (1.12.1c), the last two terms cancel out, which then establishes that indeed $\mu_i = (\partial A / \partial n_i)_{T,V,n_{j \neq i}}$.

You may use similar methods to establish that irrespective of the choice of independent variables or state functions, there exists only a single chemical potential. Ordinarily it is simplest to adopt $\mu_i = (\partial G / \partial n_i)_{T,P,n_{j \neq i}}$ as the standard definition.

Appendix: Use of Equations of State to Determine State Functions

As the first illustration, let us adopt the Berthelot equation of state for a one-component gas in the approximate form

$$P(T, V, n) = nRT/V + n^2 RTb/V^2 - n^2 a/V^2 T, \quad (1.12.26)$$

where a and b are materials-specific parameters, and n is the parametric mole number. The relation of interest involves integration of Eq. (1.12.8). For this purpose, we first need the energy derivative with respect to volume, as found from the caloric equation of state:

$$(\partial E / \partial V) = T(\partial P / \partial T) - P = 2n^2 a/V^2 T. \quad (1.12.27)$$

This relation may be integrated to yield $E(T, V, n; a) = -2n^2 a/VT + A(T, n; a)$, where A is an arbitrary function of the indicated variables. This equation could actually serve as a starting point for the rest of the derivation, but it seems pedagogically more transparent to proceed as follows: For $a = 0$, the above relation involves the ideal gas law, whence $A = E(T, 0, n; 0) = 3nRT/2$. In accord with standard convention, (Section 3.1) the ideal gas is taken as the reference state for the Berthelot gas; for a particular volume V the heat capacity is then specified by

$$C_V = 3nR/2 + 2n^2 a/VT^2. \quad (1.12.28)$$

following results when temperature and volume are changed:

Equations (1.12.27) and (1.12.28) may then be inserted in Eq. (1.12.17b) to yield the following results:

$$\begin{aligned}
E(T, V) &= E(T^*, V^*) + 3nR(T - T^*)/2 - 2n^2(a/V^*)(1/T - 1/T^*) \\
&\quad - 2n^2(a/T)(1/V - 1/V^*); \\
C_V &= 3nR/2 + 2n^2a/VT^2 + 2n^2(a/T^2)(1/V - 1/V^*); \\
(\partial E/\partial n)_{T,V} &\equiv \hat{E}(T, V) = \hat{E}(T^*, V^*) + 3R(T - T^*)/2 - 4n(a/V^*)(1/T - 1/T^*) \\
&\quad - 4n(a/T)(1/V - 1/V^*).
\end{aligned} \tag{1.12.29}$$

Note carefully that, contrary to what is sometimes asserted in the literature, one cannot always set the partial molar energy \hat{E} equal to E/n . Here, one must be careful to take partial derivatives as shown.

The entropy of the system (at constant mole number n) relative to the reference temperature T^* and composition n^* is specified via Eq. (1.12.20b)

$$\begin{aligned}
S(T, V, n) &= S(T^*, V^*, n^*) + \int_{T^*}^T \left[\frac{3nR}{T} + \frac{2n^2a}{V^*T^3} \right] dT + \int_{V^*}^V \left[\frac{nR}{V} + \frac{n^2bR}{V^2} + \frac{n^2a}{V^2T^{*2}} \right] dV \\
&= S(T^*, V^*, n^*) + \frac{3}{2}nR \ln \frac{T}{T^*} - \frac{n^2a}{V^*} \left(\frac{1}{T^2} - \frac{1}{T^{*2}} \right) + nR \ln \left(\frac{V}{V^*} \right) \\
&\quad - n^2bR \left(\frac{1}{V} - \frac{1}{V^*} \right) - \frac{n^2a}{T^{*2}} \left(\frac{1}{V} - \frac{1}{V^*} \right),
\end{aligned} \tag{1.12.30}$$

so that the partial molar entropy reads

$$\begin{aligned}
\hat{S}(T, V, n) &= \hat{S}(T^*, V, n^*) + \frac{3R}{2} \ln \left(\frac{T}{T^*} \right) + R \ln \left(\frac{V}{V^*} \right) \\
&\quad - \frac{2na}{V^*} \left(\frac{1}{T^2} - \frac{1}{T^{*2}} \right) - 2n \left(bR - \frac{a}{T^{*2}} \right) \left(\frac{1}{V} - \frac{1}{V^*} \right).
\end{aligned} \tag{1.12.31}$$

From the above, one may determine A , G , and μ by customary combinations of the above equations. Note again the technique used in this context to determine the differential entropy.

Let us next consider the case of solids for which the following equation of state holds: for monatomic solids, we adopt the high-temperature limiting form $\tilde{C}_V = 3R$; and to first order, the molar volume is given by

$$\tilde{V}(T, P) = \tilde{V}(T^*, P^*)[1 + \alpha T - \beta P]. \tag{1.12.32}$$

Using Eqs. (1.12.10a), (1.12.19b) and (1.12.20c), we arrive at

$$\begin{aligned}
\tilde{H}(T, P) &= \tilde{H}(T^*, P^*) + 3R(T - T^*) + \tilde{V}(T^*, P^*)[P - P^*] - \beta \tilde{V}(T^*, P^*)(P^2 - P^{*2})/2 \\
\tilde{S}(T, P) &= \tilde{S}(T^*, P^*) + 3R \ln(T/T^*) - \alpha \tilde{V}(T^*, P^*)[T - T^*].
\end{aligned} \tag{1.12.33}$$

Statistical Mechanics Version

We end by briefly displaying a rather different means of specifying the thermodynamic functions of state, based on elements of statistical thermodynamics that are briefly reviewed in Chapter 10 for those who need a refresher on this subject. It will be recalled that the basic building block is the molecular partition function $q = \sum_i g_i e^{-\varepsilon_i/k_B T}$, where ε_i is the i th energy level and g_i is the associated degeneracy; k_B is the Boltzmann's constant. Then the listing of Table 10.6.I provides the means of finding the desired function of state. This requires the specification via quantum mechanics of the indicated energies and degeneracies. Under the assumption that the various degrees of freedom are independent, the translational, rotational, vibrational, electronic, ... degrees of freedom are individually summed as $\varepsilon = \varepsilon_t + \varepsilon_r + \varepsilon_v + \varepsilon_e \dots$. Correspondingly, the molecular partition function is given by $q = q_t q_r q_v q_e \dots$.

- (a) For purposes of illustration, we consider here the construction of the translational partition function for an ideal gas. Along the spatial x direction quantum mechanics specifies the translational energy as

$$\varepsilon_x = n^2 h^2 / 8 m x^2, \quad n = 1, 2, 3, \dots \quad (1.12.34)$$

where m is the molecular mass, h is Planck's constant, and n is the quantum number, a positive integer; also, $g_n = 1$ for all n . Accordingly, the partition function for translation along length L_x is

$$q_x = \sum_{n=1}^{\infty} \exp\{-n^2 h^2 / 8 m L_x^2 k_B T\}. \quad (1.12.35a)$$

The spacing between consecutive energy levels is normally so small that the summation in Eq. (1.12.35a) may be replaced by an integration; exceptions occur when T or the total length along x are very small. We write

$$q_x = \int_0^{\infty} dn \exp\{-n^2 h^2 / 8 m L_x^2 k_B T\}. \quad (1.12.35b)$$

The above expression has the form of a standard Gaussian integral (Section 1.3) which converges to

$$q_x = (2\pi m k_B T / h^2)^{1/2} L_x. \quad (1.12.36a)$$

A similar expression obtains along the y and z directions. Then the overall translational partition function reads

$$q_t = q_x q_y q_z = (2\pi M k_B T / N_A h^2)^{3/2} V, \quad (1.12.36b)$$

where M is the molecular mass and N_A is the Avogadro's number. The canonical partition function (for indistinguishable particles) is then

$$\ln Q_t = N \ln q_t - N \ln N + N = N \ln(q_t e / N) = N \ln \left[\frac{(2\pi M k_B T)^{3/2} V e}{h^3 N_A^{3/2} N} \right]. \quad (1.12.37)$$

This now sets the stage for determining all the thermodynamic functions of interest. Relative to its energy at the absolute zero of temperature, the translational (molar) energy is given by

$$E_t = k_B T^2 \left(\frac{\partial \ln Q_t}{\partial T} \right)_{V,N} = \frac{3}{2} N k_B T, \quad (1.12.38)$$

which is the well-established relation showing that for each classical degree of freedom, the energy is $(1/2) N k_B T$. The enthalpy is found by adding $PV = N k_B T$, whence, relative to the same reference state, $H_t = 5 N k_B T/2$.

The molar entropy is specified³ as (using Eq. (1.12.38), and $V = \tilde{V}$, $N = N_A$),

$$\begin{aligned} \tilde{S}_t &= k_B \ln \tilde{Q}_t + \tilde{E}_t/T = \frac{3}{2} R \ln M + \frac{3}{2} R \ln T + R \ln \tilde{V} + \frac{3}{2} R + R \ln \left(\frac{(2\pi k_B)^{3/2} e}{h^3 N_A^{5/2}} \right) \\ &= \frac{3}{2} R \ln M + \frac{3}{2} R \ln T + R \ln \tilde{V} + R \ln \left(\frac{(2\pi k_B)^{3/2} e^{5/2}}{h^3 N_A^{5/2}} \right). \end{aligned} \quad (1.12.39a)$$

We can eliminate the volume term via $\tilde{V} = RT/P$ to write

$$\tilde{S}_t = \frac{3}{2} R \ln M + \frac{5}{2} R \ln T - R \ln P + R \ln \left(\frac{(2\pi k_B)^{3/2} R e^{5/2}}{h^3 N_A^{5/2}} \right), \quad (1.12.39b)$$

which is known as the *Sackur–Tetrode equation*.

The molar Helmholtz free energy relative to the energy in its standard state at $T = 0$ is specified by

$$\begin{aligned} \tilde{A}_t &= -k_B T \ln Q_t = -\frac{3}{2} RT \ln T - RT \ln \tilde{V} - \frac{3}{2} RT \ln M - RT \ln \left[\frac{(2\pi k_B)^{3/2} e}{h^3 N_A^{5/2}} \right] \\ &= -\frac{5}{2} RT \ln T - \frac{3}{2} RT \ln M + RT \ln P - RT \ln \left[\frac{R(2\pi k_B)^{3/2} e}{h^3 N_A^{5/2}} \right], \end{aligned} \quad (1.12.40)$$

and the molar Gibbs free energy relative to the energy in its standard state at $T = 0$ is found via $G = A + PV$ as

$$\tilde{G}_t = -\frac{5}{2} RT \ln T - \frac{3}{2} RT \ln M + RT \ln P - RT \ln \left[\frac{R(2\pi k_B)^{3/2}}{h^3 N_A^{5/2}} \right]. \quad (1.12.41)$$

- (b) We now consider rotational degrees of freedom: according to quantum mechanics, for a rigid linear molecule, the energy levels ε_r and degeneracies g_r and moment of inertia I_m are given by

$$\varepsilon_r = J(J+1)\hbar^2/2I_m; \quad I_m = m_a m_b r^2/(m_a + m_b); \quad g_r = 2J + 1, \quad (1.12.42)$$

where $J = 0, 1, 2, \dots$ are the integers, and the m represent the masses of the constituent atoms separated by a distance r . The rotational partition function is then given by

$$q_r = \sum_J (2J + 1) \exp[-J(J+1)\hbar^2/2I_m k_B T] \equiv \sum_j (2J + 1) \exp[-J(J+1)\Theta_r/T], \quad (1.12.43)$$

where we had defined the *characteristic rotational temperature* by the symbol $\Theta_r \equiv \hbar^2/2I_m k_B$. It turns out, however, that for a homonuclear diatomic molecule, the identity of atoms restricts the summation to either even or odd values of J . This is taken care of by introducing a symmetry number $\sigma = 2$ ($\sigma = 1$ otherwise) in the denominator. Once again, under ordinary circumstances, the spacing between adjacent rotational energy levels is small relative to $k_B T$, whence we can replace the summation by an integration. In this classical approximation, we then find that

$$q_r = \frac{1}{\sigma} \int_0^{\infty} (2J+1) \exp\left\{\frac{-J(J+1)\Theta_r}{T}\right\} dJ = \frac{T}{\sigma\Theta_r}. \quad (1.12.44a)$$

Actually, the approximation used is not completely reliable. A better relation reads as follows:

$$q_r = T/\sigma\Theta_r \{1 + \Theta_r/3T + \Theta_r^2/15T^2 \dots\}. \quad (1.12.44b)$$

The situation with polyatomic molecules is more complex. We now deal with three characteristic temperatures $\Theta_{r1,2,3} \equiv \hbar^2/2I_{m1,2,3} k_B$. For a *spherical top*, where $\Theta_{r1} = \Theta_{r2} = \Theta_{r3}$, the quantized energies are still given by Eq. (1.12.43) but the degeneracies are now $g_r = (2J+1)^2$. In the classical approximation, we find

$$\begin{aligned} q_r &= (1/\sigma) \sum_J (2J+1)^2 \exp[-J(J+1)\Theta_r/T] \\ &= (1/\sigma) \int_J (2J+1)^2 \exp[-J(J+1)\Theta_r/T] dJ. \end{aligned} \quad (1.12.45a)$$

The above may be evaluated in the approximation where J greatly exceeds 1, which is the major contribution to the integral. In that case,

$$q_r = (1/\sigma) \int_J 4J^2 \exp[-J^2\Theta_r/T] dJ = \left(\pi^{1/2}/\sigma\right) (T/\Theta_r)^{3/2}, \quad \text{spherical top} \quad (1.12.45b)$$

where the integral is again in the form of a Gaussian, which may be evaluated as shown in Section 1.3. It is fairly evident that for the remaining cases, we obtain

$$q_r = \left(\pi^{1/2}/\sigma\right) (T/\Theta_{r1})(T/\Theta_{r3})^{1/2}, \quad \text{symmetric top} \quad (1.12.45c)$$

$$q_r = \left(\pi^{1/2}/\sigma\right) (T/\Theta_{r1})^{1/2} (T/\Theta_{r2})^{1/2} (T/\Theta_{r3})^{1/2}, \quad \text{asymmetric top.} \quad (1.12.45d)$$

The principal molar thermodynamic functions of interest are now constructed by the techniques, outlined in Chapter 10. They pertain to ideal gases and to energies relative to absolute zero:

Tabulations of Molar Thermodynamic Functions for Rotations, Relative to Zero Point Enthalpy

Rigid linear molecules:

$$\tilde{E}_r = RT$$

$$\tilde{S}_r = R \ln(T/\sigma\Theta_r) + R$$

$$\tilde{G}_r = -RT \ln(T/\sigma\Theta_r)$$

Nonlinear molecules:

$$\tilde{E}_r = 3RT/2$$

$$\tilde{S}_r = R \ln \left[\left(\pi^{1/2} T^{3/2} / \sigma (\Theta_{r1} \Theta_{r2} \Theta_{r3})^{1/2} \right) \right] + R$$

$$\tilde{G}_r = -RT \ln \left[\pi^{1/2} T^{3/2} / \sigma (\Theta_{r1} \Theta_{r2} \Theta_{r3})^{1/2} \right].$$

Notice how the contribution to the molar energy for each degree of freedom is $(1/2)RT$.

- (c) We next deal with vibrational degrees of freedom. As is well established, the vibrations of a polyatomic molecule are analyzed in terms of normal coordinates that, in turn, are based on a model of independent harmonic oscillators. In short, we adopt the quantum mechanical specification

$$\varepsilon_v = \sum_{j=1}^{\alpha} (n_j + 1/2) h\nu_j, \quad n_j = 0, 1, 2, \dots, \quad (1.12.46)$$

where j specifies one of the $\alpha = 3n - 5$ or $3n - 6$ normal modes for linear or nonlinear molecules, respectively. Then the molecular partition function for one of the α modes is specified as

$$\begin{aligned} q_{v_j} &= \sum_{n_j} \exp \{ - (n_j + 1/2) h\nu_j / k_B T \} \equiv \sum_{n_j} \exp \{ - (n_j + 1/2) \Theta_{v_j} / T \} \\ &= \exp \{ - \Theta_{v_j} / 2T \} \sum_{n_j} \exp \{ - n_j \Theta_{v_j} / T \} = \frac{e^{-\Theta_{v_j}/2T}}{1 - e^{-\Theta_{v_j}/T}}, \end{aligned} \quad (1.12.47)$$

where in the top line on the right we have introduced a vibrational temperature $\Theta_{v_j} \equiv h\nu_j/k_B$ and, for convenience, in the second line have removed the constant parameters in front of the summation. The latter is an infinite sum that converges to the denominator shown on the right.

We can now determine the various thermodynamic functions of interest in the customary manner; the results are tabulated below:

Tabulations of Molar Thermodynamic Functions for Vibration

$$q_v = \prod_{j=1}^{\alpha} \frac{e^{-\Theta_{v_j}/2T}}{1 - e^{-\Theta_{v_j}/T}}.$$

$$\tilde{E}_v = R \sum_{j=1}^{\alpha} \left(\frac{\Theta_{v_j}}{2} + \frac{\Theta_{v_j}}{e^{\Theta_{v_j}/T} - 1} \right)$$

$$\tilde{S}_v = R \sum_{j=1}^{\alpha} \left[\frac{\Theta_{v_j}}{T} \frac{1}{e^{\Theta_{v_j}/T} - 1} - \ln \left(1 - e^{-\Theta_{v_j}/T} \right) \right].$$

Remark: One frequently encounters the expression for \tilde{E}_v with the first term missing. This is appropriate if the energy taken with respect to the ground state $n_j=0$, in which case the numerator in the expression for q_v is absent.

- (d) Last, we consider electronic degrees of freedom. Here no closed formulation is available; one simply begins with the listing of the energies of the molecular electronic states. The electronic ground state is set at energy zero; relative to this, the electronic energy levels are specified as

$$\varepsilon_e = g_{e0} + g_{e1}\varepsilon_{e1} + g_{e2}\varepsilon_{e2} + \dots \quad (1.12.48)$$

Normally, the excited electronic energy levels are very large compared to $k_B T$, whence it is usually sufficient to set the electronic molecular partition function as

$$q_e = g_{e0} + g_{e1}e^{-\varepsilon_1/k_B T} + g_{e2}e^{-\varepsilon_2/k_B T}, \quad (1.12.49)$$

and then use Eq. (1.12.49), as is, to determine how these electronic degrees of freedom contribute to the various thermodynamic functions of state as specified in Chapter 10.

Intervening Remark

A note of caution: The above exposition on the application of statistical mechanics is very rudimentary. While conveying the essence of the approach, the derivations apply only to highly idealized cases. We have not considered interactions among gaseous systems, rotation–vibration effects, anharmonicities in vibrations, electron interactions, and the like, which are needed for a realistic description of physical properties of actual systems. Such topics are handled in more advanced and specialized treatments in numerous textbooks on statistical mechanics, and fall outside the limited scope of the present discussion. Just be aware of the limitations inherent in the above treatment.

Statistical Treatment of Nonmetallic Solids

Nonmetallic solids will be considered as consisting of a great number of monatomic constituents held rigidly together as a lattice, and executing harmonic vibrations within their confined spaces. We neglect any internal degrees of freedom and ignore the six translational and rotational degrees of freedom of the entire rigid body, leaving us with $3N - 6 \approx 3N$ vibrational coordinates that are inserted in the partition function for the solid.

As an introduction, rewrite the expression for the molar energy of harmonic oscillators, cited above, to specify the average molar energy of a set of oscillators vibrating at a single frequency ν :

$$\tilde{E} = \tilde{E}_0 + 3R \frac{\Theta_v}{e^{\Theta_v/T} - 1}; \quad \tilde{E}_0 = \frac{3}{2} N_A h\nu, \quad \Theta_v \equiv h\nu/k_B, \quad (1.12.50)$$

where N_A is the Avogadro's number. Then the heat capacity is given by

$$\tilde{C}_V = 3R \frac{(\Theta_v/T)^2 e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2}. \quad (1.12.51)$$

This relation, commonly known as Einstein's (1905) law of heat capacities, correctly corresponds to the limiting cases $\tilde{C}_V = 0$ at $T = 0$ and to $\tilde{C}_V = 3R$ at infinite temperature—the law of Dulong

and Petit. It immediately rationalizes the deviations of the observed \tilde{C}_V values from this law at lower temperatures that had mystified scientists before the advent of quantum mechanics. However, the above equation generally deviates to some extent from experiment; in particular, at low T , the above relation shows that $\tilde{C}_V \sim T^{-2}e^{-\Theta_v/T}$, while experiments conform to a $\tilde{C}_V \sim T^3$ variation.

To accommodate these findings, Debye (1912) eliminated the unrealistic assumption that all atoms vibrate at the same fixed frequency. Since the N atoms on the crystal form a coupled system, one anticipates a spread of oscillator frequencies that needs to be introduced. For this purpose, Debye adopted the theory of a homogeneous elastic continuum, in which c_l and c_t are the velocities of one longitudinal and two transverse waves propagating in a volume V . As is well established (a euphemism for: “Everyone knows that...”), the number of frequencies in the range ν to $\nu + d\nu$ as given by the theory of elasticity is specified by

$$dZ = 4\pi V \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \nu^2 d\nu. \quad (1.12.52)$$

The total number of available frequencies is $3N$, corresponding to a range of frequencies $0 \leq \nu \leq \nu_0$. Then

$$Z = 3N = \frac{4}{3} \pi V \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \nu_0^3. \quad (1.12.53)$$

On combining Eqs. (1.12.52) and (1.12.53), we find that

$$dZ = \frac{9N}{\nu_0^3} \nu^2 d\nu, \quad (1.12.54)$$

which will now be used as the applicable distribution function for available frequencies. Then the energy of 1 mol of solid is specified by

$$\tilde{E} - \tilde{E}_0 = \frac{9R}{\nu_0^3 k_B} \int_0^{\nu_0} \frac{h\nu^3 d\nu}{e^{h\nu/k_B T} - 1} = \frac{9RT^4}{\Theta_v^3} \int_0^{\Theta_v/T} \frac{y^3 dy}{e^y - 1} = \frac{9RT}{x_D^3} \int_0^{x_D} \frac{y^3 dy}{e^y - 1}, \quad (1.12.55)$$

where $y \equiv h\nu/k_B T$, $x_D \equiv h\nu_0/k_B T$. Hence, the heat capacity is found to be

$$\frac{\tilde{C}_V}{3R} = \frac{12}{x_D^3} \int_0^{x_D} \frac{y^3 dy}{e^y - 1} - \frac{3x_D}{e^{x_D} - 1}. \quad (1.12.56)$$

The fraction in the integral can be expanded in an infinite series before the integration is attempted. The detailed execution, which involves some mathematical acrobatics, leads to the approximate result

$$\frac{\tilde{C}_V}{3R} = \frac{4}{5} \frac{\pi^4}{x_D^3} - \frac{3x_D}{e^{x_D} - 1} + \text{Correction Terms}. \quad (1.12.57)$$

At low temperatures, hence, large x_D , only the first term is of importance, which shows that the heat capacity varies as $\tilde{C}_V \sim T^3$, in good agreement with experiment.

Despite the cobbling together of elements of classical and quantum statistics, the above theory is consistently used in the analysis of data, as manifested by the empirical determination of Θ_D values for a large variety of materials. One of the saving graces is the fact that the distribution function appears under the integral sign. Hence, even considerable deviations of the real from the posited distribution function can be tolerated, without greatly changing the value of the integral in Eq. (1.12.56).

Electronic Heat Capacity of Metals

We consider the heat capacity attributed to N electrons circulating freely among N atoms that constitute a regular array of a solid. They are distributed among the N energy states of a partially filled energy band in accord with the Fermi–Dirac theory (Section 10.1) which is characterized by the Fermi energy ε_F . For a brief review of essentials, see the appendix below. Thus, at low temperatures, $k_B T \ll \varepsilon_F$, the energy required to heat N electrons from absolute zero to temperature T is given by (almost all the action involves electrons with energy at or close to ε_F)

$$E_{el}(T) = \int_{\varepsilon_F}^{\infty} d\varepsilon (\varepsilon - \varepsilon_F) f(\varepsilon; T) \rho(\varepsilon) + \int_0^{\varepsilon_F} d\varepsilon (\varepsilon_F - \varepsilon) [1 - f(\varepsilon; T)] \rho(\varepsilon). \quad (1.12.58)$$

Here $\rho(\varepsilon)$ is the density of states (DOS) in the range $d\varepsilon$ about ε ; f is the Fermi function derived in Section 10.1. The first integral represents the energy required to elevate electrons at the Fermi level to the $f(\varepsilon; T) \rho(\varepsilon)$ available energy states per unit volume at an energy $\varepsilon > \varepsilon_F$; the upper band edge energy at $W/2$ has been replaced by infinity because $\rho(\varepsilon)$ vanishes over that range. The second integral similarly shows the energy required to remove $[1 - f(\varepsilon; T)] \rho(\varepsilon)$ electrons per unit volume from energy $\varepsilon < \varepsilon_F$; to the Fermi level; the lower band edge energy at $-W/2$ has been replaced by zero, because $\rho(\varepsilon)$ vanishes in that range.

From the above, we obtain the electronic heat capacity as

$$C_{el} = (\partial E_{el} / \partial T) = \int_0^{\infty} d\varepsilon (\varepsilon - \varepsilon_F) (\partial f / \partial T) (\rho(\varepsilon)). \quad (1.12.59)$$

At low temperatures, $(\partial f / \partial T)$ differs from zero only for energies very close to ε_F ; we may thus introduce the approximation

$$C_{el} = \rho(\varepsilon_F) \int_0^{\infty} d\varepsilon (\varepsilon - \varepsilon_F) (\partial f / \partial T), \quad (1.12.60)$$

where

$$\frac{\partial f}{\partial T} = \frac{\varepsilon - \varepsilon_F}{k_B T^2} \frac{e^{(\varepsilon - \varepsilon_F)/k_B T}}{[e^{(\varepsilon - \varepsilon_F)/k_B T} + 1]^2}. \quad (1.12.61)$$

Introduce $y \equiv e^{(\varepsilon - \varepsilon_F)/k_B T}$, so that

$$C_{el} = \rho(\varepsilon_F) k_B^2 T \int_{-\varepsilon_F/k_B T}^{\infty} dy y^2 \frac{e^y}{(e^y + 1)^2}. \quad (1.12.62)$$

We may replace the lower limit by $-\infty$ without appreciable error. The resulting integral is known to converge to $\pi^2/3$; then, taking account of an additional factor of 2 for the spin degree of freedom, we obtain

$$C_{el} = \frac{2}{3} \pi^2 \rho(\varepsilon_F) k_B^2 T, \quad (1.12.63)$$

which is the final result of interest. Since the DOS is independent of T (for a free electron gas, it is specified by $\rho(\varepsilon_F) = 3Nk_B/2\varepsilon_F$), we see that within the above approximations, the electronic heat capacity rises linearly with temperature.

To the above, we now add the previously quoted Debye contribution. Then the overall heat capacity of a simple metal is given by

$$C = \gamma T + aT^3. \quad (1.12.64)$$

The correctness of this approach may be tested by noting that a plot of C/T vs T^2 should be linear, with the intercept yielding γ . The extent to which this is the case for noble metals may be seen in Figure 1.12.1. Actually, at any but the lowest temperatures, the T^3 lattice contribution swamps out the linear term; the electronic contribution is thus detectable only for, say, $T < 6$ K.

We can provide a more explicit specification for C_{el} as follows: Every quantized wave vector value \mathbf{k} is associated with a volume $(2\pi/L)^3$, as is explained in the appendix. Thus, there are $(L/2\pi)^3$ allowed \mathbf{k} values per unit volume for each allowed spin direction. Then the number of states per unit volume associated with a given set of frequencies lying in the range ν to $\nu + d\nu$ is given by the DOS relation $\rho_d(\nu)$

$$\rho_d(\nu) d\nu = \int_{S_\nu} \nu(\mathbf{k}) d^3\mathbf{k} = (L/2\pi)^3 \int_{S_\nu} d^3\mathbf{k}, \quad (1.12.65)$$

where the integration involves the set of \mathbf{k} values lying in the shell S_ν that encompasses the range ν to $\nu + d\nu$. A volume element in this shell consists of a cylinder of cross-section dA_ν and of height dk_\perp . Then $d^3\mathbf{k} = dA_\nu dk_\perp$ and the infinitesimal change in frequency is specified by $d\nu = |\nabla_{\mathbf{k}} \nu \cdot d\mathbf{k}| = |\nabla_{\mathbf{k}} \nu| dk_\perp$, so that $dk_\perp = d\nu/|\nabla_{\mathbf{k}} \nu|$. On inserting this relation in Eq. (1.12.65), we find that

$$\rho_d(\nu) d\nu = \left(\frac{L}{2\pi}\right)^3 \int dA_\nu dk_\perp = \left(\frac{L}{2\pi}\right)^3 \left(\int \frac{dA_\nu}{|\nabla_{\mathbf{k}} \nu|} \right) d\nu = \left(\frac{L}{2\pi}\right)^3 \frac{1}{|\nabla_{\mathbf{k}} \nu|} \left(\int dA_\nu \right) d\nu, \quad (1.12.66)$$

where the integral on the right reads $4\pi k^2$, so that for one electron spin direction

$$\rho_d(\nu) = \left(\frac{L}{2\pi}\right)^3 \frac{4\pi k^2}{|\nabla_{\mathbf{k}} \nu|}. \quad (1.12.67)$$

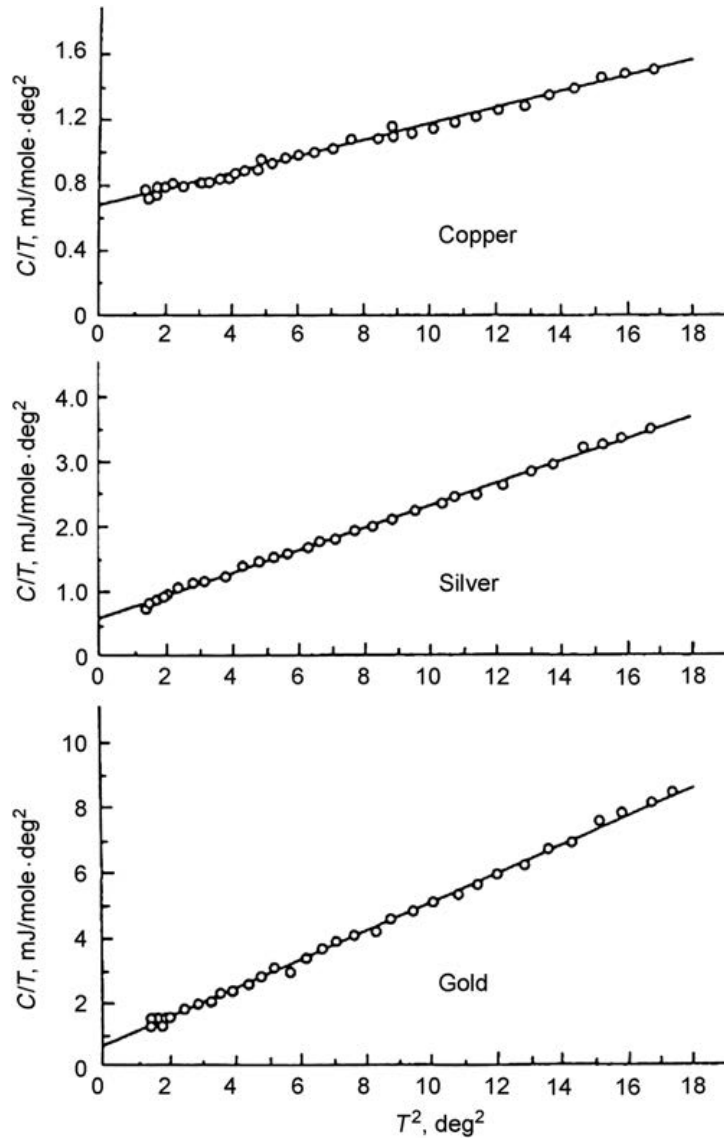


FIGURE 1.12.1

Heat capacity measurements on elemental metals at low temperature.

After W.C. Corak, M.P. Garfunkel, C.B. Satterthwaite, and A. Wexler, Phys. Rev. B98(1955) 1699.

The above relation also holds when the independent variable ν is replaced by the energy ε . On invoking $\varepsilon = \hbar^2 k^2 / 2m$ and allowing for a factor of 2 for spin degeneracy, we then see that the DOS at the Fermi energy is given by

$$\rho_d(\varepsilon_F) = \frac{2V}{(2\pi)^3} \frac{4\pi k_F^2}{\hbar^2 k_F / m} = \frac{Vm k_F}{\hbar^2 \pi^2}. \quad (1.12.68)$$

Now k_F is found by noting that in k space, a sphere of volume $4\pi k_F^3/3$ contains

$$N = 2 \frac{4\pi k_F^3/3}{(2\pi/L)^3} = \frac{V}{3\pi^2} k_F^3 \quad (1.12.69)$$

states, whence

$$k_F = (3\pi^2 N/V)^{1/3}; \quad \varepsilon_F = (\hbar^2/2m)(3\pi^2 N/V)^{2/3}. \quad (1.12.70)$$

Accordingly, the DOS at the Fermi level reads

$$\rho_d(\varepsilon_F) = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \varepsilon_F^{1/2}. \quad (1.12.71)$$

Therefore, on collecting Eqs. (1.12.63), (1.12.70) and (1.12.71), we achieve our final formulation for the free electron gas: in the limit of low temperatures,

$$C_{el} = \frac{1}{2} \pi^2 N k_B \frac{k_B T}{\varepsilon_F} = \frac{m}{\hbar^2} \left(\frac{\pi V}{3N} \right)^{2/3} N k_B^2 T. \quad (1.12.72)$$

Review of Electronic Properties of Metals

Here we insert a rudimentary review of elements of the electronic properties of metals. Quantum mechanics shows that the allowed energy levels of electrons in a periodic lattice are tightly bunched into bands that are separated by intervening “forbidden regions,” termed gaps. In the simplest case of a nondegenerate set of individual levels, for a set of N lattice atoms, each band contains exactly N quantum levels, each of which can accommodate at most two electrons with paired spins, in accord with the Pauli Exclusion Principle. The energetically lower lying bands are completely filled, the analog to completed atomic electronic shells, and are of no interest. We consider instead a higher lying band that is partially occupied by electrons. The situation for a half-filled band (N electrons occupying the $N/2$ lowest energy levels) at $T=0$ is depicted by the shaded portion of Figure 1.12.2. The cutoff energy, ε_F , is termed the *Fermi energy*. For $T > 0$, only electrons with energies $|\varepsilon - \varepsilon_F| \sim k_B T$ near the Fermi level can gain more energy in response to external stimuli; they have access to empty energy levels. The remainder is frozen in because higher lying levels beyond the range $k_B T$ are already filled.

We assume that the mobile electrons may freely travel throughout the extension of the lattice; electronic interactions may be taken into account either via an adaptation of the Debye–Hückel theory (Section 9.5) or by Spalek’s method (Section 5.12). According to quantum mechanics, the electronic wave functions are given by $\psi_{\mathbf{k}}(\mathbf{r}) = V^{-1/2} e^{i\mathbf{k} \cdot \mathbf{r}}$, where $\hbar \mathbf{k}$ is the quantized momentum vector. Allowed components of the wave vector satisfy the quantization condition $k_y = 0, \pm 2\pi/L, \pm 4\pi/L, \dots$, spaced $2\pi/L$ units apart along length L in each direction. For book-keeping purposes, the quantized \mathbf{k} are represented by a set of discrete points in \mathbf{k} space; the occupied states then all fall within a sphere of radius k_F corresponding to the energy

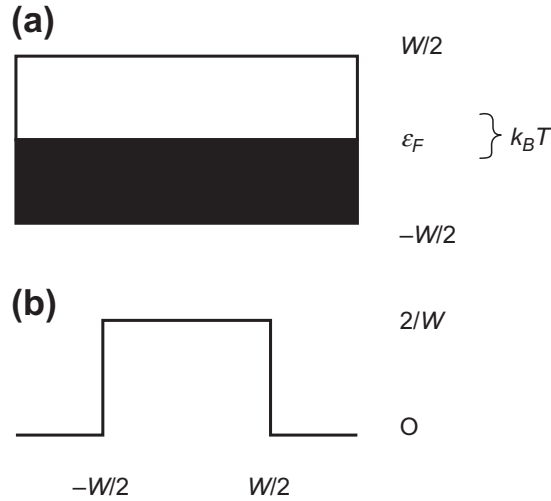


FIGURE 1.12.2

(a) Schematic representation of a half-filled simple energy band for a metallic solid. W is the band width, ε_F is the Fermi level (cutoff energy); the thermal energy of electrons $k_B T$ normally is much smaller than W . (b) Rectangular density of states corresponding to the above band.

$\varepsilon_F = p_F^2/2m_e = \hbar^2 k_F^2/2m_e$. Inside a sphere of volume $4\pi k_F^3/3$, the total number of occupied states or energy levels is therefore specified by $2(4\pi k_F^3/3)/(2\pi/L)^3 = V/3\pi^2 k_F^3 = N$, where the factor 2 arises from the allowed spin states. This then specifies $k_F = (3\pi^2 N/V)^{1/3}$, hence $\varepsilon_F = (\hbar^2/2m)(3\pi^2 N/V)^{2/3}$. However, in a band, the adjacent quantum states are so closely spaced together that \mathbf{k} is considered to be continuous.

The probability that a given energy level is occupied by an electron is provided by the *Fermi–Dirac* distribution function $f = \{\exp[(\varepsilon - \varepsilon_F)/k_B T] + 1\}^{-1}$, derived in Section 10.1. Near $T=0$, f is essentially a rectangular distribution function, with $f=1$ for $\varepsilon < \varepsilon_F$ and $f=0$ for $\varepsilon > \varepsilon_F$.

Exercises and Remark

- 1.12.1.** Carry out the necessary steps to show that all of the various chemical potentials cited in lines [5] and [6] of Table 1.12.I are in fact identical.
- 1.12.2.** From the above relations, set up expressions for the Helmholtz free energy and the chemical potential of the Berthelot gas and of the solid.
- 1.12.3.** You need to be very careful in consulting various sources on the formulation of the Sackur Tetrode equation. I have shown two apparently different looking equations, but they are identical because $3R/2 \equiv R \ln e^{3/2}$. Other sources introduce the atomic mass m in place of M/N_A or mole numbers n , which require the translation $N = nN_A$ and $NR = Nk_B$. Furthermore, it is V , not \tilde{V} , that is the appropriate factor in Eq. (1.12.37).

1.13 The Third Law of Thermodynamics

We now get to the last of the laws of thermodynamics—no more after this one (perhaps!). The third law deals with processes taking place near $T = 0$; clearly, problems arise in the determination of the entropy since the integrating factor $1/T$ diverges at zero temperature.

One must first ask whether it is possible to reach the temperature $T = 0$. For this purpose, consider a system whose deformation coordinate is represented by z , together with a conjugate variable Z , so that the element of work is given by $\delta W = -Zdz$. The energy of the system therefore is specified by $E = E(S, z) = E(S(T, z), z) = E(T, z)$, whence

$$dS = T^{-1}(dE + Zdz) = T^{-1}\{(\partial E/\partial T)dT + [Z + (\partial E/\partial z)]dz\}, \quad (1.13.1)$$

Now take second derivatives of S with respect to z and T in either order; this yields

$$(\partial/\partial z)[T^{-1}(\partial E/\partial T)] = (\partial/\partial T)\{T^{-1}[Z + (\partial E/\partial z)]\}. \quad (1.13.2)$$

After carrying out the indicated differentiations, one obtains

$$(Z + \partial E/\partial z) = T(\partial Z/\partial T). \quad (1.13.3)$$

Now apply Eq. (1.13.1) to an adiabatic and reversible process; it is only under such conditions that one can hope to achieve ultralow temperatures. On setting $dS = 0$, Eq. (1.13.1) becomes

$$dT = -[\{(Z + (\partial E/\partial z))\}/(\partial E/\partial T)]dz, \quad (1.13.4)$$

whence, by Eq. (1.13.3),

$$dT = -T[(\partial Z/\partial T)_z/(\partial E/\partial T)_z]dz \equiv -[T(\partial Z/\partial T)_z/C_z]dz. \quad (1.13.5)$$

The above expression carries an important general message: in any adiabatic process that produces a change of thermodynamic coordinates z , the temperature of the system is necessarily altered or the process incurs a phase change.

In general, there appears to be no reason why the temperature cannot be lowered arbitrarily as long as $(\partial Z/\partial T)_z/C_z$ is positive. However, it is an experience of mankind that as $T \rightarrow 0$, C_z varies with temperature as T^{-a} , $a \geq 1$. Since $C_z > 0$, everything thus hinges on whether $(\partial Z/\partial T)_z > 0$ approaches zero faster than does the quantity T^{1-a} which diverges at the limit $T = 0$. It emerges experimentally that this is always the case. Therefore, $T(\partial Z/\partial T)_z/C_z$ vanishes at the limit $T = 0$, making it impossible to reach this limit.¹

This conclusion has ramifications: since the differential of the Helmholtz free energy $A = E - TS$ is given by $dA = -Zdz - SdT$, the cross-differentiation with respect to z and T gives rise to a Maxwell relation of the form $(\partial Z/\partial T)_z = (\partial S/\partial z)_T$, whence Eq. (1.13.5) may be rewritten as

$$dT = -(T/C_z)(\partial S/\partial z)_T dz. \quad (1.13.6)$$

Notice that since the limit $T = 0$ is unattainable, one must require that in every conceivable situation, $(\partial S/\partial z)_T T/C_z \rightarrow 0$ as $T \rightarrow 0$. Thus, $(\partial S/\partial z)_T$ not only approaches zero but does so faster than $1/T^{a-1}$.

Furthermore, the statement $(\partial S/\partial z)_T \rightarrow 0$ as $T \rightarrow 0$ is incorporated in another law: the third law of thermodynamics asserts that

as any system approaches the lowest possible temperature of 0 K the entropy of the system assumes a particular, least value when the system is in its lowest energy state. The entropy reaches this value with zero slope, taken with respect to all thermodynamic deformation coordinates.

One should carefully note that there is no claim that S itself vanishes at $T = 0$. The statement about lowest energy attends to the fact that in the cooling process to lowest temperatures, excited energy states may accidentally be frozen in. This then keeps the system from attaining equilibrium, which then cannot be properly characterized solely in terms of deformation coordinates. Also, any equilibrium state that remains intrinsically disordered as $T \rightarrow 0$ will have a nonzero entropy; examples are furnished in the Remarks section.²

By way of summary, according to the third law, a system in its lowest energy state is also in its most stable configuration; its entropy at absolute zero, S_0 , has the lowest possible value, for every coordinate z under consideration. Moreover, the lowest possible entropy is attained in the limit of vanishing slope: $(\partial S/\partial z)T \rightarrow 0$ as $T \rightarrow 0$.

Despite the above disclaimer, one often does set $S_0 = 0$; this may be done whenever S_0 remains unaltered during a given process. As a simple example, consider processes that do not involve nuclear transformations. Here, the entropy at $T = 0$ associated with the mixture of different isotopic species does not change. Hence, for practical purposes, we may ignore the isotopic contribution, thereby allowing us to set the effective entropy at $T = 0$ to zero. However, one must obviously be very careful in determining whether setting $S_0 = 0$ is justified; some counterexamples are offered in the Remarks section.²

An important consequence of the third law is that it denies the existence of an ideal gas. For, as we establish later in Section 2.4, its entropy is given by

$$S = C_V \ln T + R \ln V, \quad (1.13.7)$$

whose derivative, $(\partial S/\partial V)_T = R/V$ does not vanish at $T = 0$. This fact, of course, does not prevent us from using the ideal gas law as an approximation to characterize properties of actual gases at higher temperatures. However, it is clear that the approximation fails at low T .³

Remarks and Queries

- 1.13.1. Statements in the literature referring to negative temperatures in connection, for example, with NMR experiments with population inversion, will not be included here because they always involve nonequilibrium configurations of the system under study.
- 1.13.2. Exceptions to setting $S_0 = 0$ arise whenever configurational disorder must be taken into account, as for a material that remains disordered or is in several states of equal energy that are frozen in at $T = 0$. Several instances come to mind. (a) Helium, which remains a liquid at $T = 0$, unless subjected to external pressure. (b) Solid CO, H₂O, N₂O and the like: neighboring pairs may be encountered in configurations such as CO–CO or CO–OC of nearly equal energy. At ultralow temperatures, even that small energy difference may become important, and a disordered state is frozen in. On heating, the disorder is annihilated. (c) Glasses or solid mixtures such as AgCl + AgBr that may be regarded as frozen liquids or solutions, with a residual entropy of mixing that is taken up in later

chapters. (d) Paramagnetic materials whose electronic spins in the absence of external magnetic fields remain disordered down to lowest attainable temperatures. (e) Materials in which it is important to take account of isotopic distributions or nuclear spin degeneracies, if these quantities change in a given process.

- 1.13.3.** There is also a logical problem in the elementary derivations of the second law that are quoted in many textbooks. These depend on the use of an ideal gas as a working substance in Carnot cycles that are then used in setting up the second law. Clearly, it is awkward to have to acknowledge at a later stage that the very existence of such a working substance is denied by the third law.
- 1.13.4.** Does the van der Waals or Berthelot equation of state satisfy the requirements of the third law? Discuss the implications of your answer.

1.14 The Gibbs–Duhem Relation and Its Analogs

So far we have not dealt with the question about how changes in composition of a system affect our thermodynamic analysis. We now undertake such a study. As a first example, consider the manner in which the volume of a system depends on its chemical constitution at constant temperature and pressure. The latter are then parameters in the problem—quantities that are fixed for a given experimental situation but that may be appropriately altered when the experimental conditions change. Thus, for fixed T and P , we want the volume to be a homogeneous function of the mole numbers n ($i = 1, 2, \dots, r$) of the constituents of the system: doubling the mole numbers of all constituents doubles the volume of the system. This allows us to cite Euler's theorem (Section 1.3) in the form

$$V(T, P; n_1, n_2, \dots, n_r) = \sum_{i=1}^r n_i (\partial V / \partial n_i)_{T, P, n_{j \neq i}}. \quad (1.14.1)$$

For convenience, we now introduce $\bar{V}_i \equiv (\partial V / \partial n_i)_{T, P, n_{j \neq i}}$ as a short-hand notation to write

$$V(T, P; n_1, n_2, \dots, n_r) = \sum_{i=1}^r n_i \bar{V}_i(T, P, n_i). \quad (1.14.2)$$

Here \bar{V}_i is known as the *partial molal volume of component i*. It represents the effective volume of component i in a mixture of r constituents at temperature T and pressure P ; alternatively, it is the incremental increase in volume of the mixture when the i th component is added in infinitesimal amounts at constant temperature and pressure, while keeping all other components at fixed values. In general, the volume of the mixture is not equal to the sum of volumes of the individual components in their pure states. We show below one technique for determining the individual \bar{V}_i experimentally.

A Variant on the Gibbs–Duhem Relation

As discussed above, the volume of a system is an analytic function of the form $V = V(T, P; n_1, n_2, \dots, n_r)$ with T and P as variable parameters. Its total differential form reads

$$dV = (\partial V / \partial T)_{P, n_i} dT + (\partial V / \partial P)_{T, n_i} dP + \sum_{i=1}^r \bar{V}_i dn_i, \quad (1.14.3)$$

which is to be compared with the differential obtained from Eq. (1.14.2):

$$dV = \sum_{i=1}^r \bar{V}_i dn_i + \sum_{i=1}^r n_i d\bar{V}_i. \quad (1.14.4)$$

Consistency then demands that we set

$$\sum_{i=1}^r n_i d\bar{V}_i = (\partial V / \partial T)_{P, n_i} dT + (\partial V / \partial P)_{T, n_i} dP, \quad (1.14.5a)$$

which, for fixed T and P , reduces to

$$\sum_{i=1}^r n_i d\bar{V}_i = 0. \quad (1.14.5b)$$

The above relations represent variants on the *Gibbs–Duhem relation* in the form of *constraints*. One cannot independently change T , P , and the summation $\sum_{i=1}^r n_i d\bar{V}_i$. This has repercussions on relation Eq. (1.14.3) that are not obvious, and that must be individually examined as shown later.

Determination of Partial Molal Volumes

The determination of partial molal volumes shown below provides another illustration of thermodynamic methodology. We begin by defining the molar volume of a mixture as $\tilde{V} \equiv V / \sum_i n_i$. In terms of mole fractions, rewrite Eq. (1.14.2) as

$$\tilde{V} = \sum_i x_i \bar{V}_i. \quad (1.14.6)$$

It is evident that for a one-component system, $\tilde{V}_1 = \bar{V}_1$.

Specializing now to a two-component system, differentiate the function $\tilde{V} = (1 - x_2)\bar{V}_1 + x_2\bar{V}_2$:

$$\begin{aligned} (\partial \tilde{V} / \partial x_2)_{T, P} &= -\bar{V}_1 + (1 - x_2)(\partial \bar{V}_1 / \partial x_2)_{T, P} + \bar{V}_2 + x_2(\partial \bar{V}_2 / \partial x_2)_{T, P} \\ &= -\bar{V}_1 + x_1(\partial \bar{V}_1 / \partial x_2)_{T, P} + \bar{V}_2 + x_2(\partial \bar{V}_2 / \partial x_2)_{T, P}. \end{aligned} \quad (1.14.7)$$

To simplify the sum of the second and fourth terms, note that at constant T and P , $\bar{V}_i = \bar{V}_i(x_1, x_2)$; then return to Eq. (1.14.5b), which specializes to

$$x_1 \left[\left(\frac{\partial \bar{V}_1}{\partial x_1} \right) dx_1 + \left(\frac{\partial \bar{V}_1}{\partial x_2} \right) dx_2 \right] + x_2 \left[\left(\frac{\partial \bar{V}_2}{\partial x_1} \right) dx_1 + \left(\frac{\partial \bar{V}_2}{\partial x_2} \right) dx_2 \right] = 0 \quad T, P \text{ const.} \quad (1.14.8)$$

To ensure that this sum does vanish, it is sufficient to demand that

$$\left[x_1 \left(\frac{\partial \bar{V}_1}{\partial x_2} \right) + x_2 \left(\frac{\partial \bar{V}_2}{\partial x_2} \right) \right] dx_2 = \left[x_1 \left(\frac{\partial \bar{V}_1}{\partial x_1} \right) + x_2 \left(\frac{\partial \bar{V}_2}{\partial x_1} \right) \right] dx_1 = 0. \quad (1.14.9)$$

This then reduces Eq. (1.14.7) to the form

$$(\partial \tilde{V} / \partial x_2)_{T, P} = \bar{V}_2 - \bar{V}_1. \quad (1.14.10a)$$

Next, set $\tilde{V} = x_1 \bar{V}_1 + x_2 \bar{V}_2$ and eliminate \bar{V}_2 by use of Eq. (1.14.10a), whence

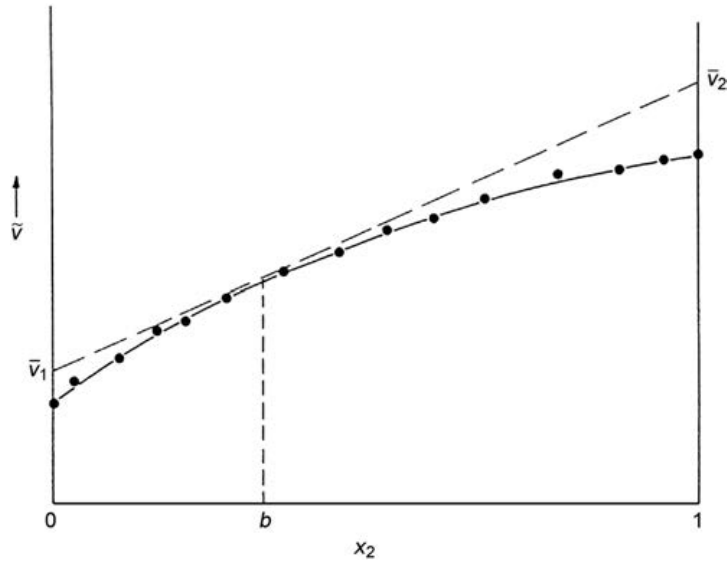


FIGURE 1.14.1

Plot illustrating how the partial molal volumes of components in a binary mixture may be determined by extrapolation.

$$\bar{V}_1 = \tilde{V} - x_2 \left(\partial \tilde{V} / \partial x_2 \right)_{T,P}. \quad (1.14.10b)$$

Similarly, it may be shown that

$$\bar{V}_2 = \tilde{V} + (1 - x_2) \left(\partial \tilde{V} / \partial x_2 \right)_{T,P}. \quad (1.14.10c)$$

This provides a means for finding the partial molal volumes, as shown in Figure 1.14.1. One measures the molar volume of the solution at a set of x_2 values. At a particular value $x_2 = b$, a tangent to the curve is drawn. The points of intersection of this tangent at $x_2 = 0$ and 1 yield the desired quantities \bar{V}_1 and \bar{V}_2 , respectively. Other methods for finding partial molal volumes are cited in textbooks and in the literature; see also Ref. 2.

The Gibbs–Duhem Relation

A very important application of the concept of partial molal quantities relates to the Gibbs free energy in the form $G = G(T, P; n_1, n_2, \dots, n_r)$. Since this function is to be homogeneous in the mole numbers n_i we proceed by strict analogy to the above treatment of effective volumes. For a one-component system, the Gibbs free energy obeys $G = n_1 \bar{G}_1$. For multicomponent systems, this generalizes to $G = \sum_i \bar{G}_i n_i$ where \bar{G}_i represents the effective Gibbs free energy of component i in the mixture at constant T and P , or, the change in the Gibbs free energy when an infinitesimal amount of component i is added to the mixture at constant T , P , and with constant mole numbers of the other components. We satisfy the Euler criterion by writing

$$G(T, P; n_1, n_2, \dots, n_r) = \sum_{i=1}^r n_i \mu_i(T, P; n_1, n_2, \dots, n_r), \quad (1.14.11a)$$

where

$$\mu_i \equiv (\partial G / \partial n_i)_{T,P,n_{j \neq i}} \quad (1.14.11b)$$

is the familiar chemical potential. The differential form of Eq. (1.14.11a) is specified by

$$dG = \sum_i n_i d\mu_i + \sum_i \mu_i dn_i, \quad (1.14.12a)$$

which is to be compared to the analytic differential form for the Gibbs function, $G(T,P;n_1,n_2,\dots,n_r)$, namely,

$$dG = (\partial G / \partial T)_{P,n_i} dT + (\partial G / \partial P)_{T,n_i} dP + \sum_{i=1}^r \mu_i dn_i. \quad (1.14.12b)$$

We thus establish that

$$\sum_i n_i d\mu_i = (\partial G / \partial T)_{P,n_i} dT + (\partial G / \partial P)_{T,n_i} dP = -SdT + VdP, \quad (1.14.13a)$$

which at constant T and P specializes to

$$\sum_i n_i d\mu_i = 0. \quad (1.14.13b)$$

Both expressions are known as the *Gibbs–Duhem relation*. When equilibrium prevails, all differential quantities in Eqs. (1.14.13a) and (1.14.13b) vanish and these relations are fulfilled identically. However, when applied to infinitesimal changes in properties of the system, the above relations are not trivial. They show that in executing reversible changes, T , P , and the μ_i cannot be changed in an arbitrary manner. Equation (1.14.13) then becomes constraining relations that govern and restrict the processes to those that are executed in conformity with the above requirements. The above expressions are also useful in checking on the consistency of any formulation of the Gibbs free energy. Examples of such restrictions will be furnished later. G is not as readily measured as V ; hence, methods other than those for specifying partial molal volumes must be used to determine the chemical potentials. These procedures will also be taken up at a later stage.

Query and Reference

- 1.14.1. Provide an example of a system for which the following statement is *incorrect*: consider two systems at the same temperature and pressure containing the same chemical materials in identical amounts. When these are combined, the total energy is twice that of each subsystem. What does this teach you? Explain in detail what conditions must be met so that the statement is corrected.
- 1.14.2. J.M. Honig *Thermodynamics* (Academic Press, Amsterdam, 2007) 3rd Ed., p. 91.

1.15 Heat Capacities; Fundamentals and Applications

Heat Capacities at Constant Volume and Constant Pressure

Here, we have a look at how heat capacity measurements may be used to derive a number of useful results. We begin with a study of the relation between heat capacity at constant volume and at constant pressure; it provides another excellent example of the consistent application of thermodynamic interrelations. The result is also of practical interest: for, the quantity better suited for theoretical analysis is C_{V,n_i} , whereas it is simpler to measure heat capacities at constant pressure, C_{P,n_i} ; the volume always changes with temperature, rendering constant volume control problematic.

We relate the two heat capacities starting with the enthalpy $H = E + PV$; for simplicity, we assume that the composition of the system remains fixed; thus,

$$C_P = (\partial H / \partial T)_P = (\partial E / \partial T)_P + P(\partial V / \partial T)_P. \quad (1.15.1)$$

Also, as in Eq. (1.12.6), set $E = E(T, V)$, so that

$$\partial E = (\partial E / \partial T)_V dT + (\partial E / \partial V)_T dV = C_V dT + (\partial E / \partial V)_T dV. \quad (1.15.2)$$

Next, differentiate with respect to T at constant P (the coefficients remain unaffected (Section 1.3)). Thus,

$$(\partial E / \partial T)_P = C_V + (\partial E / \partial V)_T (\partial V / \partial T)_P. \quad (1.15.3)$$

Insert Eq. (1.15.3) into Eq. (1.15.1) to obtain

$$C_P = C_V + [P + (\partial E / \partial V)_T] (\partial V / \partial T)_P. \quad (1.15.4)$$

Now invoke Eq. (1.12.7b) to write

$$C_P = C_V + T(\partial P / \partial T)_V (\partial V / \partial T)_P. \quad (1.15.5)$$

It is difficult to measure $(\partial P / \partial T)_V$ because V cannot readily be kept fixed while varying T . Accordingly, we use Eq. (1.3.8) to write

$$\left(\frac{\partial P}{\partial T} \right)_V = - \frac{(\partial V / \partial T)_P}{(\partial V / \partial P)_T}. \quad (1.15.6)$$

Insertion into Eq. (1.15.5) finally leads to

$$C_P - C_V = -T \frac{(\partial V / \partial T)_P^2}{(\partial V / \partial P)_T} \equiv \frac{\alpha^2 V T}{\beta}. \quad (1.15.7)$$

Here $\alpha = V^{-1}(\partial V / \partial T)_P$ is the *isobaric expansion coefficient* of the material, and $\beta = -V^{-1}(\partial V / \partial P)_T$ is its *isothermal compressibility*. These two parameters are usually tabulated as a function of temperature, so that the difference $C_P - C_V$ can be determined.

It is readily checked that for an ideal gas,

$$C_P - C_V = nR, \quad (1.15.8)$$

where n is the number of moles of gas and R is the gas constant.

As a second example, we turn to heat capacity measurements carried out adiabatically. As mentioned in Section 1.13, such processes change the temperature of the system. We investigate an infinitesimal step during which pressure is altered adiabatically and reversibly. The response is governed by the differential function

$$\left(\frac{\partial T}{\partial P}\right)_S = -\frac{(\partial S/\partial P)_T}{(\partial S/\partial T)_P} = \frac{T}{C_P} \left(\frac{\partial V}{\partial T}\right)_P, \quad (1.15.9)$$

where we had invoked Eqs. (1.3.8), (1.12.7a) and entry [8] in Table 1.12.II. Once again, knowledge of the function $V(T,P)$ and of the temperature dependence of C_P suffice to determine the quantity of interest. In a similar manner, one may prove that

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V} = -\frac{T}{C_V} \left(\frac{\partial P}{\partial T}\right)_V = \frac{T}{C_V} \frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}. \quad (1.15.10)$$

where Eq. (1.15.6) was introduced on the right. As was emphasized in connection with the third law, any adiabatic change in deformation coordinates results in a change of temperature unless phase transitions are involved. Equations (1.15.9) and (1.15.10) show the extent of such a change in terms of quantities that are experimentally accessible.

The variation of heat capacity with pressure¹ or volume at constant composition is given by $\partial^2 S/\partial T \partial P = (1/T)(\partial C_P/\partial P)_T = -(\partial^2 V/\partial T^2)_P$, whence

$$(\partial C_P/\partial P)_T = -T(\partial^2 V/\partial T^2)_P, \quad (1.15.11)$$

and similarly

$$(\partial C_V/\partial V)_T = T(\partial^2 P/\partial T^2)_V. \quad (1.15.12)$$

Once more, the equation of state may be used to explore the indicated partial derivatives.

The Joule–Thomson Effect

One of the good illustrations of thermodynamic methodology is based on the Joule–Thomson porous plug experiment; the results were also of considerable practical interest in the latter half of the nineteenth century, at a time when the liquefaction of gases became of great importance. Consider the passage of a gas through a porous plug in an adiabatically insulated enclosure, supplied with moveable pistons, as shown schematically in Figure 1.15.1. Let the gas initially be in volume V_1 and at pressure P_1 on the left and let it be completely transported quasi-statically at constant pressure through the porous plug. Let it emerge on the right where the pressure is maintained at the constant value P_2 and where the final volume is V_2 . This process is isenthalpic: for, the work involved in moving the gas through the porous plug (surroundings) from the left (energy diminishing) is given by $W_1 = -\int_{V_1}^0 P_1 dV = P_1 V_1$, while the work involved on the right is specified by taking the inverse of W_1 : $W_2 = \int_{V_2}^0 P_2 dV = -P_2 V_2$. The net work is then given by $W = W_1 + W_2 = P_1 V_1 - P_2 V_2 = \Delta E = E_2 - E_1$, since $Q = 0$. Thus, $E_2 + P_2 V_2 = H_2 = E_1 + P_1 V_1 = H_1$. Therefore, the process, known as the *Joule–Thomson porous plug experiment* is isenthalpic, as claimed. It is characterized by the *Joule–Thomson coefficient*,

$$\eta_J \equiv (\partial T/\partial P)_H, \quad (1.15.13)$$

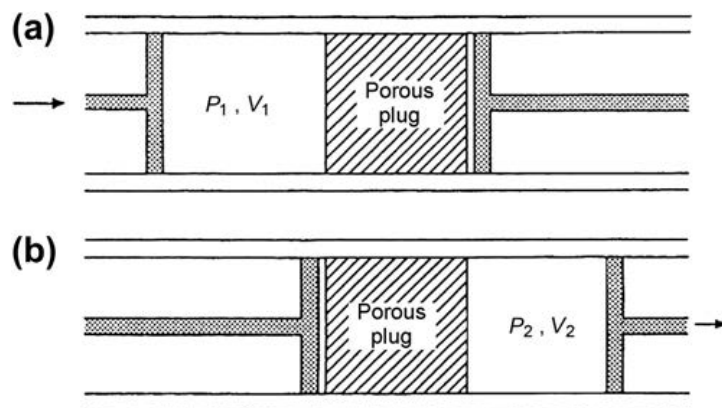


FIGURE 1.15.1

Porous plug experiment of Joule and Thomson. (a) Initial state: the gas is on the left in volume V_1 and at pressure P_1 . A pressure P slightly greater than P_1 is applied to the piston to drive the gas through the porous plug. (b) Final state: the gas has been reversibly and under isenthalpic conditions forced through the plug and appears on the right-hand side in volume V_2 and at pressure $P_2 < P_1$.

which correlates the change in temperature of the gas as it passes through a pressure difference across the porous plug. Depending on whether $\eta_J > 0$, $\eta_J = 0$, or $\eta_J < 0$, a gas will either cool, remain at constant temperature, or heat up as it passes through the plug (N.B. dP is negative). We examine the magnitude and sign of η_J using the van der Waals gas as an illustrative example.

We first adopt Eq. (1.3.8) to rewrite Eq. (1.15.13) in the form

$$\eta_J = -\frac{(\partial H/\partial P)_T}{(\partial H/\partial T)_P} = -\frac{(\partial H/\partial P)_T}{C_P}. \quad (1.15.14)$$

Introduce Eq. (1.12.10b) into the expression $(\partial H/\partial P)_T = -\eta_J C_P$ to obtain (on a molar basis; $\tilde{V} \equiv V/n$; $\tilde{C} \equiv C/n$)

$$T(\partial \tilde{V}/\partial T)_P - \tilde{V} = \eta_J C_P. \quad (1.15.15)$$

We now adopt the van der Waals equation of state:

$$P = RT/(\tilde{V} - b) - a/\tilde{V}^2. \quad (1.15.16)$$

Unfortunately, its inversion to obtain $\tilde{V}(T, P)$ for insertion in Eq. (1.15.15) is algebraically very cumbersome. We thus resort to approximations. Multiply both sides of Eq. (1.15.16) by $\tilde{V} - b/P$ to obtain

$$\tilde{V} = RT/P - a/P\tilde{V} + b + ab/P\tilde{V}^2. \quad (1.15.17)$$

We regard the last three terms as “corrections” to the perfect gas law, and in this spirit, replace \tilde{V} on the right-hand side by RT/P , whence

$$\tilde{V} = RT/P - a/RT + b + abP/(RT)^2. \quad (1.15.18)$$

Then

$$(\partial \tilde{V} / \partial T)_P = R/P + a/RT^2 - 2abP/R^2T^3. \quad (1.15.19)$$

Now solve Eq. (1.15.18) for R/P and substitute the result in Eq. (1.15.19) to obtain

$$(\partial \tilde{V} / \partial T)_P = (\tilde{V} - b)/T + 2a/RT^2 - 3abP/R^2T^3. \quad (1.15.20)$$

When Eqs. (1.15.18) and (1.15.20) are inserted in Eq. (1.15.15) one finds, on neglect of the term involving $1/T^3$:

$$\eta_J = (1/\tilde{C}_P)(2a/RT - b - 3abP/R^2T^2). \quad (1.15.21)$$

This is the final equation of interest; it determines the sign of η_J . Where the third term does not dominate, η_J is rendered positive for “large” a and for “small” b , i.e., for large interatomic forces and for small effective volumes. In addition, the heat capacity should be as small as possible. These requirements must be optimized to achieve the liquefaction of gases by cooling. However, as the pressure is raised, the third term in Eq. (1.15.21) becomes increasingly important, and ultimately causes η_J to pass through zero and then turn negative. Hence, the operating pressure drop across the porous plug must be chosen carefully to ensure conditions of gas liquefaction.

Inversion Temperature

A practical problem of interest is to determine the *inversion temperature*, T_i , at which $\eta_J = 0$. According to Eq. (1.15.21), this happens when T_i satisfies the quadratic equation

$$T_i^2 - (2a/Rb)T_i + 3ab/R^2 = 0. \quad (1.15.22)$$

A plot of T_i vs P , as applied to N_2 gas, is shown in Figure 1.15.2. The calculated curve is in fair agreement with experiment. Better agreement is achieved by use of more realistic approximations to the equation of state. Somewhere below 350 bar, there exist two inversion temperatures that are specified by Eq. (1.15.22). For all temperatures within the curve, η_J remains positive; this maps out the conditions that must be satisfied for effective cooling of a gas via adiabatic expansion through a porous plug.

Isenthalps¹

Isenthalps can be used to establish the enthalpy of a van der Waals gas at any point in its adiabatic expansion through the porous plug. We begin with the expression [for the remainder of this section, all extensive quantities will be specified as being molar variables] $dH = (\partial H / \partial T)_P dT + (\partial H / \partial P)_T dP$, whence

$$dH = C_P(T, P)dT - C_P\eta_J dP = C_P(T, P)dT + [-2a/RT + b + 3abP/R^2T^2]dP. \quad (1.15.23)$$

Since dH is an exact differential, the cross-derivatives taken in either order must match

$$\left(\frac{\partial C_P}{\partial P} \right)_T = \frac{2a}{RT^2} - \frac{6abP}{R^2T^3}. \quad (1.15.24)$$

Next, carry out an indefinite integration over pressure at constant temperature:

$$C_P = (2a/RT^2)P - (3ab/R^2T^3)P^2 + L(T), \quad (1.15.25)$$

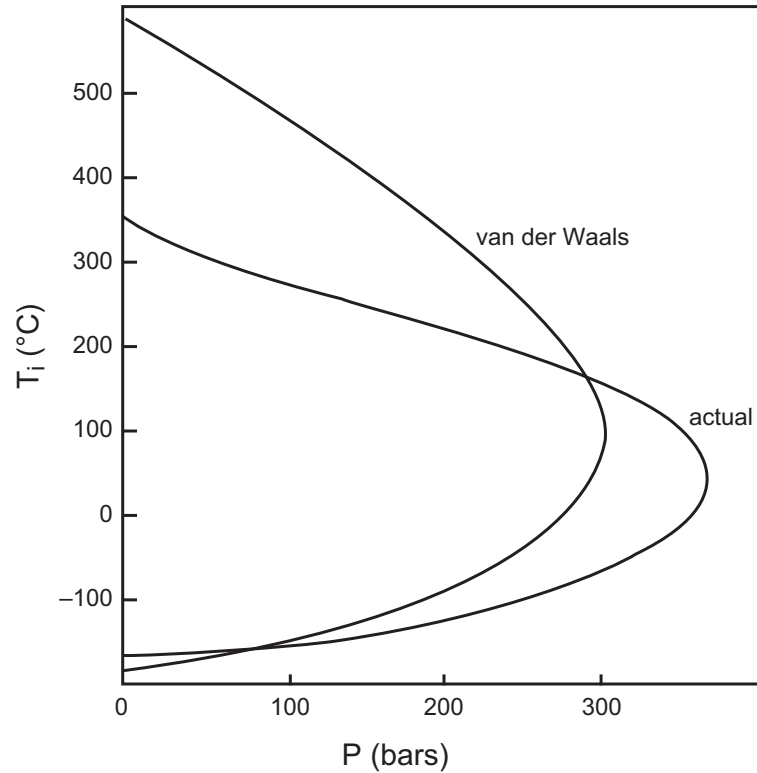


FIGURE 1.15.2

Joule–Thomson inversion curve for N_2 gas; actual data as compared to predictions based on the van der Waals equation state.

where $L(T)$ is an arbitrary, unspecified function of the temperature. Then, by combining Eqs. (1.15.2), (1.15.11) and (1.15.13), the Joule–Thomson coefficient may be written as

$$\eta_J = -\frac{1}{C_P} \left(\frac{\partial H}{\partial P} \right)_T = \frac{2a/RT - 3abP/R^2T^2 - b}{L(T) + (2a/RT^2)P - (3ab/R^2T^3)P^2} \approx \frac{2a/RT - b}{L(T) + (2a/RT^2)P}, \quad (1.15.26)$$

where the higher order terms have been dropped.

Let the van der Waals gas be taken from an initial state T_1, P_1 to a final state T_2, P_2 in two steps. (i) Cool the gas reversibly from T_1 to T_2 at constant pressure P_1 . (ii) Expand the gas reversibly from P_1 to P_2 at fixed temperature T_1 . In executing these steps under these conditions, we find on use of Eqs. (1.15.23) and (1.15.25):

$$\begin{aligned} 0 = \Delta H &= \int_{T_1}^{T_2} C_P dT|_{P_1} + \int_{P_1}^{P_2} dH|_{T_2} \\ &= \int_{T_1}^{T_2} \left[\frac{2aP_1}{RT^2} - \frac{3abP_1^2}{R^2T^3} + L(T) \right] dT + \int_{P_1}^{P_2} \left[-\frac{2a}{RT_2} + \frac{3abP}{R^2T_2^2} + b \right] dP. \end{aligned} \quad (1.15.27)$$

On dropping out higher order terms and taking a , b , and L to be sensibly independent of temperature, we can carry out the integration to obtain

$$0 = \Delta H = -\frac{2aP_1}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) + L(T_2 - T_1) + \left[b - \frac{2a}{RT_2} \right] (P_2 - P_1). \quad (1.15.28)$$

This may be rearranged to read

$$\begin{aligned} LT_1 + bP_1 - (2a/R)(P_1/T_1) &= LT_2 + bP_2 - (2a/R)(P_2/T_2) = H(T_1, P_1) \\ &= H(T_2, P_2) \equiv H, a \text{ constant.} \end{aligned} \quad (1.15.29)$$

Thus, the quantity

$$H(T, P) = -(2a/R)(P/T) + LT + bP \quad (1.15.30)$$

is a constant under the assumed conditions and approximations and represents the desired isenthalp. Equation (1.15.29) can be used to determine the variation of temperature with pressure, given a , b , H , and L . Equation (1.15.25) may be used to fix L experimentally, and to check whether this quantity is in fact independent of T . If this is not the case, the $L(T)$ dependence must be introduced in Eq. (1.15.27) before the integration is performed. In the present case, H is found by insertion of one pair of P and T values. Having thus fixed H , Eq. (1.15.29) is then employed again to trace out the general dependence of T on P . Note that, on account of Eq. (1.15.25), the slope of this curve furnishes a value of η_J for each specified set of (P, T) values. The maximum of the slope for each H curve thus determines the largest accessible value of the Joule–Thomson coefficient for a given set of conditions.

In numerical work, recall the approximations that have been introduced. More accurate results are obtained by introducing fewer restrictive assumptions and more realistic equations of state.

Aside from its intrinsic interest, the above discussion furnishes a nice illustration of how the methodology of thermodynamics can be used to obtain results of practical value.

Heat Measurements and Calorimetry

Earlier, heat has been treated as a somewhat aetherial quantity, having been introduced as a deficit function that restores the balance between energy changes and work performance in a system. Subsequently, we reintroduced heat in conjunction with the concept of entropy. We now complement the earlier presentations with a more meaningful description by introducing a set of units and a method for measuring heat transfers.

The *heat* transfer was originally measured in units of calories, where *one calorie* was defined as the quantity of energy required to raise 1 g of pure water from 14.5 to 15.5 °C at 1 atm. This definition has been supplanted by the introduction of the *joule*, which represents the energy specified by the conversion factor: 1 cal = 4.184 J. One joule is also equivalent to the energy developed in a circuit by an electric current of 1 A flowing through a resistance of 1 Ω (driven by a potential difference of 1 V) in 1 s.

Heat transfers are conveniently measured by calorimetric techniques. At constant composition, we write

$$dE = (\partial E / \partial T)_V dT + (\partial E / (\partial V)_T) dV. \quad (1.15.31)$$

At constant volume, the second term drops out and the partial derivative in the first term represents the heat capacity at constant volume, C_V . Then, in the absence of any other work for an infinitesimal step, we may write

$$dE = \delta Q|_V = C_V dT, \quad (1.15.32a)$$

and in a finite step,

$$\Delta E = Q|_V = \int_{T_1}^{T_2} C_V dT = \langle C_V \rangle (T_2 - T_1), \quad (1.15.32b)$$

where the quantity in angular brackets represents an averaged value. Thus, the heat generated by a given process in an adiabatically insulated calorimeter may be determined by the temperature rise, once the heat capacity of the apparatus is known. This may be found by supplying a known amount of electrical energy to the system and recording the temperature increase of the calorimeter. Naturally, the actual procedures of calibration and operation are much more involved than indicated. In fact, one cannot easily measure temperature increases at constant volume. Hence, we now consider processes at constant pressure.

For this purpose, one invokes Eq. (1.12.10a) to establish that (for fixed P and in the absence of any work)

$$dH = \delta Q|_P = C_P dT \quad (1.15.33a)$$

and

$$\Delta H = Q|_P = \int_{T_1}^{T_2} C_P dT = \langle C_P \rangle (T_2 - T_1). \quad (1.15.33b)$$

Here the temperature changes are monitored at constant pressure, so that thermal expansion problems are moot.

There exist many other techniques for determining heat generation and transfer, which you are invited to explore by reference to appropriate texts and monographs. The principal purpose of the present discussion is only to outline one method by which Q or changes in energy and enthalpy may be measured.

Entropy Determinations via Calorimetry

One of the important problems in thermodynamics involves the determination of the entropy of any material. Here we introduce the use of calorimetry for this purpose. Before taking up this question, we must examine the characteristics of phase transitions.

Consider a material that undergoes a first-order phase transition such as fusion, vaporization, allotropic transformation, and the like. In each case, two phases remain in equilibrium at a fixed temperature while heat flows in or out of the system during the transition. The theoretical background for characterizing this process will be provided in Chapter 2.

The energy change of the system on completion of the transition is specified by (in the absence of any work other than mechanical)

$$\Delta E_t = Q_t + W_t = Q_t - \int_t PdV. \quad (1.15.34)$$

Transitions are generally carried out at constant pressure; we thus replace the integral by $P\Delta V_t$ and then obtain

$$\Delta H_t|_P = Q_t|_P. \quad (1.15.35)$$

The corresponding entropy change on completion of the transition is found by invoking $\Delta H = T\Delta S$ at equilibrium,⁵ so that for the change in phase

$$\Delta S_t|_P = \Delta H_t|_P/T_t. \quad (1.15.36)$$

Henceforth we drop the P subscript. We also reintroduce $(\partial S/\partial T)_P = (C_P/T)$, to write

$$S_2 - S_1 = \int_{T_1}^{T_2} (C_P/T) dT = \int_{T_1}^{T_2} C_P d \ln T. \quad (1.15.37)$$

Now let's get back to the main topic. Consider a material whose entropy is to be determined as a function of increasing temperature. Let the sample undergo an $\alpha\beta$ transition at temperature $T_{\alpha\beta}$, melt at a temperature $T_m > T_{\alpha\beta}$, and boil at a temperature $T_b > T_m$. We wish to determine the entropy at a temperature $T > T_m$. For convenience, we divide the temperature interval into distinct segments $0 \rightarrow T_a \rightarrow T_{\alpha\beta} \rightarrow T_m \rightarrow T_b \rightarrow T$; here T_a is the temperature somewhere in the range 0–10 K, below which it is difficult to determine C_P accurately. We proceed by considering the various ranges separately.

Between 0 and T_a one frequently resorts to the Debye theory, Eq. (1.12.57) for the heat capacity of a nonconducting solids, and extended to metals by Sommerfeld. As a first approximation, one uses the relation Eq. (1.12.72):

$$C_P = aT^3 + \gamma T, \quad (1.15.38)$$

where a and γ are the parameters that are specified by microscopic theories, as shown in Section 1.12. In practice, their values are usually determined empirically by plotting C_P vs T^2 ; the straight line has a slope a and intercept γ . Figure 1.15.3 shows the three such plots for the indicated elemental metals; these show the degree to which the present analysis is applicable, and the extent of extrapolation required to determine the intercept. Inserting Eq. (1.15.38) into Eq. (1.15.37), we write

$$S(T_a) - S(0) = \int_0^{T_a} (aT^2 + \gamma) dT = \frac{aT_a^3}{3} + \gamma T_a. \quad (1.15.39a)$$

As an aside, $S(0)$ vanishes only under the conditions prescribed in Section 1.13.

In the range T_a to $T_{\alpha\beta}$, we set

$$S(T_{\alpha\beta}) - S(T_a) = \int_{T_a}^{T_{\alpha\beta}} (C_P^\alpha/T) dT, \quad (1.15.39b)$$

that requires an empirical determination of C_P^α as a function of T for phase α , so that the integration may be performed.

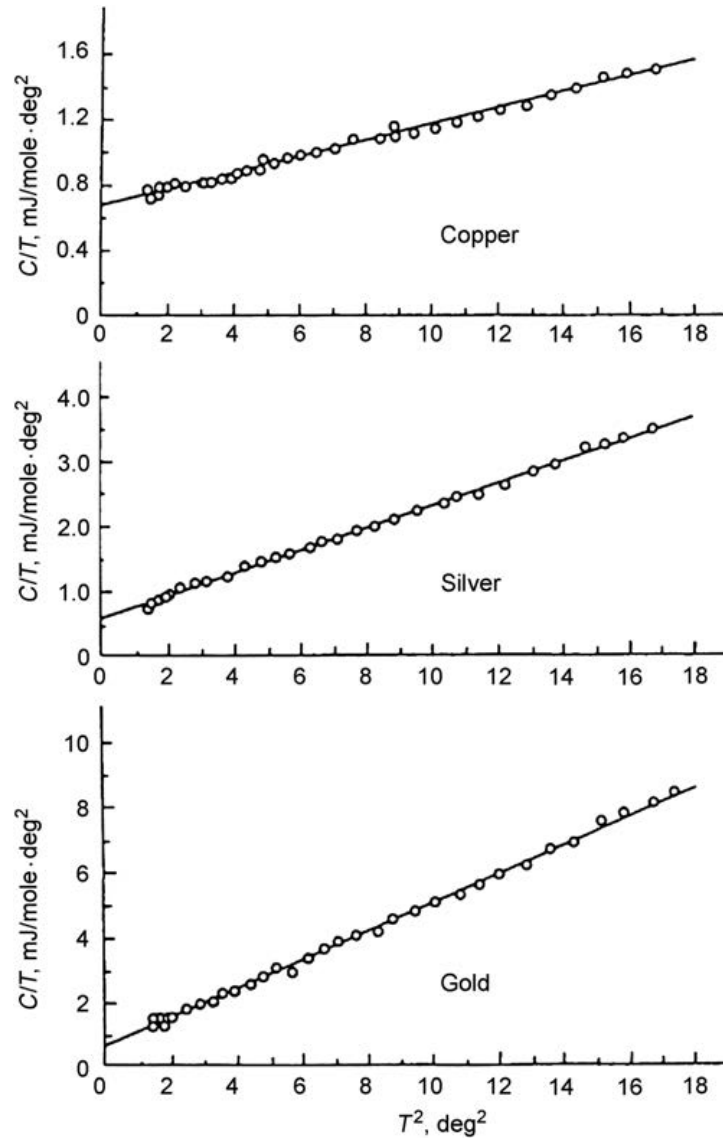


FIGURE 1.15.3

Heat capacity measurements on elemental metals at low temperature.

After W.C. Corak, M.P. Garfunkel, C.B. Satterthwaite, and A. Wexler, Phys. Rev. B98(1955) 1699.

At the $\alpha\beta$ phase transition, we write

$$(S_\beta - S_\alpha)_{T_{\alpha\beta}} = Q_{\alpha\beta}/T_{\alpha\beta} = \Delta H_{\alpha\beta}/T_{\alpha\beta}. \quad (1.15.39c)$$

The entropy change in the range $T_{\alpha\beta}$ to T_m is given by

$$S(T_m) - S(T_{\alpha\beta}) = \int_{T_{\alpha\beta}}^{T_m} (C_P^\beta/T) dT. \quad (1.15.39d)$$

It is evident that the remaining contributions are as follows:

$$(S_l - S_s)_{T_m} = Q_m/T_m = \Delta H_m/T_m \quad (\text{at the melting point}) \quad (1.15.39e)$$

$$S(T_b) - S(T_m) = \int_{T_m}^{T_b} (C_P^l/T) dT \quad (\text{for the liquid phase}) \quad (1.15.39f)$$

$$(S_v - S_l)_{T_b} = Q_b/T_b = \Delta H_b/T_b \quad (\text{at the boiling point}) \quad (1.15.39g)$$

$$S(T) - S(T_b) = \int_{T_b}^T (C_P^v/T) dT \quad (\text{for the gas phase}). \quad (1.15.39h)$$

We then find $S(T) - S(0)$ by addition of Eqs. (1.15.39a)–(1.15.39h). While this is straightforward, the difference $S(T) - S(0)$ depends on the pressure to the same extent that C_P , Q , and the various temperature ranges do. It is therefore conventional to measure, or at least report, all results under *standard conditions* of 1 bar and to let users of such information introduce corrections such as the use of entry [7], Table 1.12.II to determine $S(T)$ at other pressures via the equation of state. Conventionally, entropies cited for standard conditions are denoted by $S^0(T)$.

It should be evident that a similar approach is used to find the enthalpy. Beginning with Eqs. (1.15.35) and (1.15.38), we obtain under standard conditions

$$H^0(T) - H^0(0) = aT_a^4/4 + \gamma T_a^2 + \int_{T_a}^{T_{\alpha\beta}} C_P^{\alpha 0} dT + Q_{\alpha\beta}^0 + \int_{T_{\alpha\beta}}^{T_m} C_P^{\beta 0} dT + \dots \quad (1.15.40)$$

We may combine the above to determine the standard Gibbs free energy according to

$$G^0(T) - H^0(0) = (H^0(T) - H^0(0)) - T(S^0(T) - S^0(0)). \quad (1.15.41)$$

Tabulations of $\frac{[G^0(T) - H^0(0)]}{T}$, $\frac{[H^0(T) - H^0(0)]}{T}$ and of $S^0(T) - S^0(0)$ are available in numerous reference works in the literature and play a large role in industrial applications.

By way of illustrations, we display in Figure 1.15.4 a plot of the molar heat capacity of oxygen under standard conditions. The plot of C_P vs $\ln T$ is then used to determine the entropy of oxygen from the area under the curves. Note that the element in the solid state exists in three distinct allotropic modifications, with transition temperatures close to 23.6 and 43.8 K; the melting point occurs at 54.4 K, and the boiling point is at 90.1 K. All the enthalpies of transition at the various phase transformations are accurately known. An extrapolation procedure was employed below 14 K, which in 1929 was about the lower limit that could then conveniently be reached in calorimetric measurements.

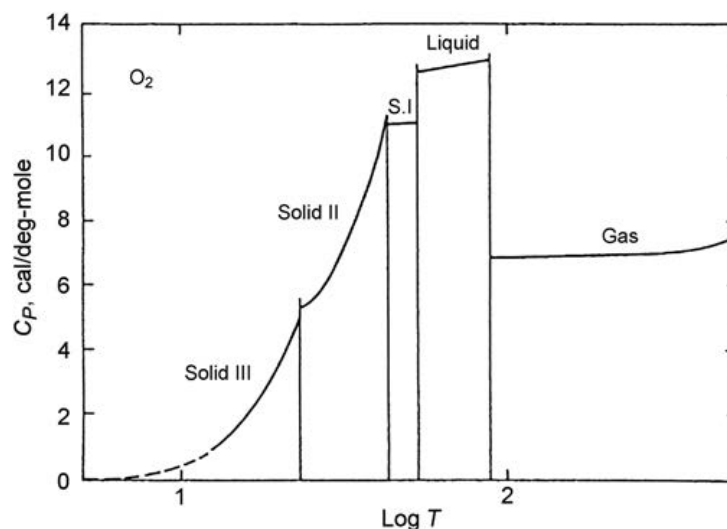


FIGURE 1.15.4

The molar heat capacity of oxygen.

After W.F. Giauque and H.L. Johnston, J. Amer. Chem. Soc. 51(1929) 2300.

Acknowledgment

1.15.1. The author is greatly indebted to Professor James W. Richardson at Purdue University for useful discussions that formed the basis for formulating the present section.

Exercises and Comments

- 1.15.1.** Is it not a contradiction of terms to differentiate C_p , the heat capacity at constant pressure, with respect to pressure? How do you resolve this apparent problem?
- 1.15.2.** Determine the variation of C_p with P and of C_v with V for an ideal gas and for a van der Waals gas. Comment on your findings.
- 1.15.3.** Determine the dependence of T on P and on V for isentropic processes using an ideal gas. Note the resulting expressions.
- 1.15.4.** Repeat Exercise 1.15.2, using the van der Waals gas as a working substance. In carrying out the mathematical manipulations, do not attempt to solve the van der Waals equation for $V(T, P)$ but use appropriate mathematical “tricks” of Section 1.3, so that you can always employ the van der Waals equation in the form $P = P(T, V)$.
- 1.15.5.** Here we are getting slightly ahead of the logical presentation. In Chapter 2, we learn that two phases—1 and 2—at equilibrium are characterized by the same Gibbs free energy: $F_1 = H_1 - T_1 S_1 = F_2 = H_2 - T_2 S_2$. These findings are not based on arguments developed in the present section; hence, the reasoning is not circular.

1.16 Effect of Chemical Changes on the Energy of a System¹

So far we have made no distinction between changes in mole numbers of constituent i that are brought about by transport of i across the system boundaries (n_i) and those arising from chemical reactions that occur totally within the system (N_i). To handle this case in preliminary fashion, let us provisionally amend the first law to read

$$dE = TdS - PdV + \sum_j \mu_j dn_j + \sum_i \mu_i dN_i. \quad (1.16.1)$$

Consider the special case of a closed system with $dn_j = 0$ for all j . The resulting expression

$$dE = TdS - PdV + \sum_i \mu_i dN_i \quad (1.16.2)$$

must be handled with care.²

By way of illustration, consider a set of reagents in the isolated system whose mole numbers N_i are initially kept fixed by constraints. Then let the constraints be lifted so that interactions may take place *reversibly*, adiabatically, and at fixed volume, without transfer of material across the boundaries. *If* this can be achieved by an arrangement such as in Note 1.16.2, then $dS = dE = 0$, which in turn requires that

$$\sum_i \mu_i dN_i = 0. \quad (1.16.3)$$

This conclusion clearly shows that chemical processes occurring entirely within a system can be dispensed with in considering energy changes brought about by reactions. This result is perfectly in accord with the statements of Section 1.7; any process occurring totally within the boundaries of a system does not change its energy. The chemical reactions considered in the following chapters always involve reagents imported from external sources; these react within the reaction chamber, and the reaction products are then delivered to exterior receptacles.

This brings up the question about characterizing slow spontaneous reactions such as the conversion of hydrogen and oxygen into water at room temperature in the absence of catalysts or outside interference. Here, energy is still conserved but the entropy of the system increases, no matter how slowly the process takes place. To achieve reversibility, one must set up inside the system elaborate, baroque constructs such as illustrated in Remark 1.16.2 that are hardly ever present under actual operating conditions. In the absence of such operations, Eq. (1.16.2), which tacitly invokes the assumption of reversibility, is no longer applicable and must be supplanted by the machinery of Section 1.9 and/or Chapter 6. In Chapter 2, we show that Eq. (1.16.3) is in fact equivalent to the specification of equilibrium conditions as applied to chemical reactions. Under conditions illustrated in Remark 1.16.2, any isochoric reaction, carried out by itself very slowly under strictly isolated conditions, generates an internal entropy change $dS \equiv d\theta = \sum_i \mu_i dN_i > 0^3$; nevertheless $dE = 0$.

Remarks

1.16.1. The author thanks Professor Dor Ben Amotz of Purdue University for very insightful discussions concerning this topic.

- 1.16.2.** The problem that arises may be illustrated as follows: 2 mol of hydrogen gas and 1 mol of oxygen gas are placed in a totally isolated container initially at room temperature. The reaction that forms water as a condensed phase proceeds exceedingly slowly. So why should Eq. (1.16.3) not apply to this case? The resolution hinges on what is meant by a reversible reaction. Even though the reaction itself proceeds very gradually, no provision has been made that would enable one to bring the system back to its original state, let alone without incurring any other changes in the universe. The process is therefore spontaneous, with $dS \equiv d\theta > 0$, and Eq. (1.16.3), which is based on the assumption of reversibility, is no longer applicable. This indicates that the execution of a very slow reaction is a necessary but by no means sufficient condition to indicate reversibility. To achieve the latter, one may, for example, include in the isolated system an interactive electrochemical cell (Chapter 4) that is very slowly charged by the execution of the reaction. When the chemical process is terminated, the initial conditions may be restored by slowly running the cell backward. In this specially constructed system, the total entropy change is represented by $dS_r + dS_c = 0$, where the two symbols stand for the entropy change in an infinitesimal step of the reaction and of the cell. More generally, to ensure reversibility of a chemical reaction, one must include in the isolated system some type of storage unit to which the thermodynamic changes in the reaction may be reversibly transferred, and from which they may be recovered in the same manner by the reverse process. It is in this sense that the quantity $dS \equiv (dS_r + dS_c)$ used in the text must be understood when dealing with isolated systems since the usual differential relations for functions of state only apply under reversible conditions. In other words, the quantity dS in Eq. (1.16.2) is determined only in part by the reversible heat transfers across the boundaries, and, as already indicated, does include the entropy change brought about by a purely irreversible, internal rearrangement of atoms in the absence of external influences. Irreversible phenomena must be treated as outlined in Section 1.9 or Chapter 6.
- 1.16.3.** This, then also resolves the problem raised earlier in conjunction with the explosive reaction of hydrogen and oxygen in an adiabatic, rigid container. Here the energy change of the system is indeed zero, but the process is characterized by an increase in the entropy of the system. However, the explosive release of the reaction cannot, of course, be handled by the machinery of this chapter. Rather, since entropy is a function of state, we can substitute the equivalent reaction as carried out by a reversible process (see above) to determine the entropy change. For this purpose, we invoke the theory of Section 2.9.

1.17 Stability of a System; Fluctuations

Let us now veer away from the study of reversibility by investigating the effects of stability constraints and of fluctuations. This is motivated by the fact that a system in a quiescent state is not really inert. Rather, as shown below, and is well substantiated experimentally and by statistical mechanics and quantum theory, any system (even at the absolute zero of temperature) exhibits erratic fluctuations about the mean values of all thermodynamic properties. We want to characterize these fluctuations in the context of thermodynamic stability.

Generalized Legendre Transforms

We introduce the subject by considering a thermodynamic function of state Y which involves $n + 1$ independent *extensive* variables x_0, x_1, \dots, x_r which are conjugate to a corresponding set p_0, p_1, \dots, p_r of *intensive* variables. We are interested in constructing a new thermodynamic function of state Z , in which the first $n + 1$ extensive quantities x_i ($i = 0, 1, \dots, n$) are replaced by their intensive counterparts p_i ($i = 0, 1, \dots, n$). To achieve this objective we introduce the (partial) Legendre transform as follows:

$$Z(p_0, p_1, \dots, p_n; x_{n+1}, \dots, x_r) = Y(x_0, x_1, \dots, x_r) - \sum_{i=0}^n p_i x_i, \quad (1.17.1)$$

in which the p_i on the right and the differential form of Y are specified by

$$p_i = \left(\frac{\partial Y_i}{\partial x_i} \right)_{x_{j \neq i}}, \quad dY = \sum_{i=0}^r p_i dx_i. \quad (1.17.2)$$

The differential forms of Eq. (1.17.1) then are given by

$$dZ(p_0, p_1, \dots, p_n; x_{n+1}, \dots, x_r) = dY((x_0, x_1, \dots, x_r)) - \sum_{i=0}^n p_i dx_i - \sum_{i=0}^n x_i dp_i. \quad (1.17.3)$$

On introducing Eq. (2) we then find that

$$dZ(p_0, \dots, p_n; x_{n+1}, \dots, x_r) = - \sum_{i=n+1}^r p_i dx_i - \sum_{i=0}^n x_i dp_i, \quad (1.17.4)$$

Accordingly, where Eq. (1.17.1) had been introduced. Then

$$\begin{aligned} \left(\frac{\partial Z(p_0, \dots, p_n; x_{n+1}, \dots, x_r)}{\partial p_k} \right)_{p_{j \neq k}} &= -x_k \quad (k \leq n), \\ \left(\frac{\partial Z(p_0, \dots, p_n; x_{n+1}, \dots, x_r)}{\partial x_k} \right)_{x_{j \neq k}} &= p_k \quad (k > n). \end{aligned} \quad (1.17.5)$$

Now from Eq. (1.17.2) we note that

$$\left(\frac{\partial p_k}{\partial x_k} \right)_{x_{j \neq k}} = \left(\frac{\partial^2 Y}{\partial x_k^2} \right)_{x_{j \neq k}}. \quad (1.17.6)$$

For comparison, carry out a second differentiation in Eq. (1.17.5):

$$\left(\frac{\partial^2 Z}{\partial p_k^2} \right)_{p_{j \neq k}} = - \left(\frac{\partial x_k}{\partial p_k} \right)_{p_{j \neq k}} = - \frac{1}{(\partial^2 Y / \partial x_k^2)_{x_{j \neq k}}} \quad (k \leq n). \quad (1.17.7)$$

In a mouthful of words, a sign change occurs when one switches from taking second derivatives of a function of state (Y) with respect to extensive variables, to taking second derivatives of the Legendre transformed function of state (Z) with respect to the conjugate intensive variables. This mathematical relationship must be clearly kept in mind what now follows.

General Stability Conditions

Consider a system for which the energy function is specified by $E(S, V, n_1, \dots, n_r)$. It is perfectly conceivable in principle to construct a very rigid enclosure so that its volume V remains constant under all operations. Likewise, we can arrange things, so that we maintain the composition within the enclosure constant. Nevertheless, there will take place fluctuations in entropy or energy of the system that correspond to slight erratic departures from equilibrium. To handle the energy fluctuations, we expand E in a Taylor series about its equilibrium value E_0 :

$$E - E_0 = (\partial E / \partial S)|_{0, V, n_k} dS + (1/2)(\partial^2 E / \partial S^2)|_{0, V, n_k} d^2 S + \dots, \quad (1.17.8)$$

where the zero subscript serves as a reminder that the derivatives are to be evaluated in the limit of zero fluctuations, i.e., for the true equilibrium state E_0 of the energy. Therefore, the first derivative vanishes, and the second must be positive so that E be at a minimum value consistent with the fixed constraints; we exclude here and below the trivial case $dS = d^2 S = 0$. Thus, on account of Eqs. (1.12.1a) and (1.12.7a),

$$(\partial^2 E / \partial S^2)|_{0, V, n_k} = (\partial T / \partial S)_{V, n_k} = T / C_{V, n_k} > 0. \quad (1.17.9a)$$

This shows first that the entropy at constant volume and composition rises with temperature, as should be the case; second, the heat capacity at constant volume and composition cannot be negative.

Similarly, if the volume of a flexible system is allowed to fluctuate under adiabatic conditions (*henceforth, the subscript 0 will be omitted*):

$$(\partial^2 E / \partial V^2)_{S, n_k} = -(\partial P / \partial V)_{S, n_k} > 0. \quad (1.17.9b)$$

As before, the inequality obtains because at equilibrium, the energy is at a minimum under the indicated constraints. To satisfy this requirement, the first derivative must be negative: $(\partial P / \partial V)_{S, n_k} < 0$; under adiabatic processes at constant composition any pressure rise in an isotropic medium produces a shrinkage of volume—a common sense experience.

Last, in view of Eq. (1.12.1a), fluctuations in composition under adiabatic and isochoric conditions (arising, for example, through fluctuations in equilibrated chemical equations, triggered by temperature fluctuations) are subject to the constraint that at equilibrium E is at a minimum:

$$(\partial^2 E / \partial n_i^2)_{S, V, n_{j \neq k}} = (\partial \mu_i / \partial n_i)_{S, V, n_{j \neq k}} > 0. \quad (1.17.9c)$$

This indicates that the chemical potential of species i rises as more i is added to the system at constant S , V , and constant $n_{j \neq i}$ —a common feature of all potential functions. In view of all of the above, whatever the extensive variable, E remains convex.

We next apply this method to the enthalpy $H = H(T, P, n_i)$: Since at equilibrium, H is at a minimum, we find that (Eqs. (1.12.1b) and (1.12.10a))

$$(\partial^2 H / \partial S^2)_{P, n_k} = (\partial T / \partial S)_{P, n_k} = T / C_{P, n_k} > 0. \quad (1.17.10a)$$

Again, a rise in temperature raises the entropy of the system during a process at constant pressure and composition. Also, the heat capacity at constant pressure and composition cannot be negative.

Adiabatic fluctuations in H with the intensive variable P at constant composition must, however, be handled inconformity with Eq. (1.17.7):

$$(\partial^2 H / \partial P^2)_{S, n_i} = -(\partial^2 E / \partial V^2)_{S, n_i}^{-1} = (\partial V / \partial P)_{S, n_i} < 0, \quad (1.17.10b)$$

which is identical with Eq. (1.17.9b).

Lastly, consider

$$(\partial^2 H / \partial n_i^2)_{S, P, n_{j \neq i}} = (\partial \mu_i / \partial n_i)_{S, P, n_{j \neq i}} > 0, \quad (1.17.10c)$$

with the same message as Eq. (1.17.9c), except that constant pressure conditions prevail.

In a similar vein, one may derive relations that invoke Eq. (1.17.7), as needed when fluctuations of intensive variables are considered:

$$(\partial^2 A / \partial T^2)_{V, n_i} = -(\partial^2 E / \partial S^2)_{V, n_i}^{-1} = -(\partial S / \partial T)_{V, n_i} = -C_{V, n_i} / T < 0, \quad (1.17.11a)$$

showing that $C_{V, n_i} > 0$, in conformity with Eq. (1.17.9a). Furthermore, when extensive variables are involved, A is subject to the relation

$$(\partial^2 A / \partial V^2)_{T, n_i} = -(\partial P / \partial V)_{T, n_i} = (V\beta)^{-1} > 0, \quad (1.17.11b)$$

showing that the isothermal compressibility function β , as commonly defined, is positive. This relation is the constant $-T$ analog of Eq. (1.17.9b). Finally,

$$(\partial^2 A / \partial n_i^2)_{T, V, n_{j \neq i}} = (\partial \mu_i / \partial n_i)_{T, V, n_{j \neq i}} > 0, \quad (1.17.11c)$$

which is the analog of Eq. (1.17.9c); again, the chemical potential increases with mole number of species i under the indicated constraints.

Lastly, we consider the Gibbs free energy; by Eq. (1.17.10a)

$$(\partial^2 G / \partial T^2)_{P, n_i} = -(\partial^2 H / \partial S^2)_{P, n_i}^{-1} = -(\partial S / \partial T)_{P, n_i} = -C_{P, n_i} / T < 0. \quad (1.17.12a)$$

showing that at constant composition and pressure, the entropy rises with temperature, and that C_{P, n_i} is positive, as already established in Eq. (1.17.10a). Also,

$$(\partial^2 G / \partial P^2)_{T, n_i} = -(\partial^2 A / \partial V^2)_{T, n_i}^{-1} = (\partial V / \partial P)_{T, n_i} < 0, \quad (1.17.12b)$$

as already established in Eq. (1.17.11b), while

$$(\partial^2 G / \partial n_i^2)_{T, P, n_{j \neq i}} = (\partial \mu_i / \partial n_i)_{T, P, n_{j \neq i}} > 0, \quad (1.17.12c)$$

which is the pressure analog of Eq. (1.17.11c).

Virtual Processes in Closed Systems

We next consider virtual energy changes in a closed system. As before, the second-order term in the expansion of $E = E(S, V)$ must be positive to guarantee stability; we avoid the trivial case $dS = dE = 0$. Now introduce the symbols $E''_{SS} \equiv (\partial^2 E / \partial S^2)_V$ and similarly for the other partial derivatives. The stability condition then reads

$$\delta^2 E = (1/2) \left[E''_{SS} (\delta S)^2 + 2E''_{SV} \delta S \delta V + E''_{VV} (\delta V)^2 \right] > 0. \quad (1.17.13)$$

In Appendix A1, we show that the following conditions must apply to satisfy the requirement $\delta^2 E > 0$:

$$E''_{SS} > 0; E''_{VV} > 0; E''_{SS} E''_{VV} - (E''_{SV})^2 > 0. \quad (1.17.14)$$

The first two conditions duplicate Eqs. (1.17.9a) and (1.17.9b). The third condition assumes the form

$$(E''_{SV})^2 < -T(\partial P / \partial V)_{S, n} / C_V. \quad (1.17.15)$$

The positive right-hand side furnishes both an upper and a negative lower bound for the cross-derivative E''_{SV} . If desired, the quantity $(\partial P / \partial V)_S$ may be rewritten via Eq. (1.3.8) in terms of partial derivatives that involve the entropy.

Similar arguments may be advanced for virtual changes involving the other thermodynamic functions of state. However, one must be careful: for example, virtual changes in the Helmholtz function are governed by relations such as Eq. (1.17.11a) that require a sign reversal. Accordingly,

$$\delta^2 A = (1/2) \left[A''_{TT} (\delta T)^2 + 2A''_{TV} \delta T \delta V + A''_{VV} (\delta V)^2 \right] > 0, \quad (1.17.16)$$

Hence, we write Eqs. (1.17.11a) and (1.17.11b)

$$-A''_{TT} = (\partial S / \partial T)_V = C_V / T > 0; A''_{VV} = -(\partial P / \partial V)_T = \beta V > 0, \quad (1.17.17)$$

in conformity with Eqs. (1.17.11a) and (1.17.11b). Also,

$$(A''_{TV})^2 < (-A''_{TT})(A''_{VV}) = (\partial S / \partial T)_P (-\partial P / \partial V)_T = C_P / \beta VT, \quad (1.17.18)$$

which establishes an upper and a negative lower bound for the cross-derivative.

You should take the time and trouble to use the above arguments to find the second derivatives of the enthalpy and of the Gibbs free energy functions so as to establish analogs of Eqs. (1.17.13, 1.17.14, 1.17.17 and 1.17.18).

General Theory of Fluctuations

So far we have dealt with inequalities. Complementary to the above, additional interesting information becomes available on considering fluctuations as an object of intrinsic interest.

Here we follow the methodology of Waldram.¹ We first introduce the Gaussian distribution function for a variable x whose deviation from its mean value \bar{x} is of interest. For a uniform distribution of x values, the probability of encountering a particular x value in the distribution is given by the normalized Gaussian relation,

$$\varphi_\sigma(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(x - \bar{x})^2}{2\sigma^2}\right), \quad (1.17.19)$$

where $\sigma^2 \equiv \langle (x - \bar{x})^2 \rangle \equiv \langle \Delta x^2 \rangle$ is defined as the *variance*.

We next introduce the statistical definition for the entropy as developed in Chapter 10. In following the formulation by Boltzmann, S is related to the probability of occupation of available microstates. However, of greater relevance to our later treatment is the probability of occupancy of states in a small

range of energies dE centered on E when the state of the system also depends on a variable x which fluctuates in the range dx about x . Accordingly, under conditions specified in Chapter 10, for sufficiently large systems we can relate S to the energy-dependent distribution function $f(x, E) = \ln g(x, E)$, Eq. (10.7.15), such that the *molar* entropy \tilde{S} , to an excellent degree of approximation, is specified by

$$\tilde{S} = R \ln g(x, E). \quad (1.17.20)$$

Here $g(x, E)$ is the appropriate DOS of the system that characterizes fluctuations of dx about energies x while the system is subject energy conservation. A trivial rearrangement of the above relation leads to

$$f(x) \equiv g(x, E) = e^{\tilde{S}(x)/R}. \quad (1.17.21)$$

Since fluctuations in entropy for large systems are expected to be small, we now expand \tilde{S} as a Taylor series in x about the neighborhood of its equilibrium value $\tilde{S}(x_0)$:

$$\tilde{S} = \tilde{S}(x_0) + (\partial\tilde{S}/\partial x)_{x=x_0}(x - x_0) + (1/2)(\partial^2\tilde{S}/\partial x^2)_{x=x_0}(x - x_0)^2 + \dots \quad (1.17.22)$$

The derivatives are to be evaluated under equilibrium conditions, where \tilde{S} is a maximum; hence, the first derivative drops out. Invoking Eq. (1.17.21), we are left with

$$f(x) \propto \exp \left[\left(\frac{1}{2} \frac{\partial^2 \tilde{S}}{\partial x^2} \right)_{x=x_0} \Delta x^2 / R \right], \quad (1.17.23)$$

which has the form (1.17.19), with the variance specified as

$$\langle \Delta x^2 \rangle = - \frac{R}{(\partial^2 \tilde{S} / \partial x^2)_{x=x_0}}. \quad (1.17.24)$$

Equation (1.17.24) is the fundamental relation of interest; parenthetically, since \tilde{S} is a maximum at $x = x_0$, the second derivative is negative, rendering $\langle \Delta x^2 \rangle$ positive, as required. Since this quantity is to be evaluated for the system in the absence of fluctuations, the machinery of equilibrium thermodynamics may be used to determine the second derivative.

Examples: Systems at Constant Volume and Composition

As always, one must carefully track the constraints imposed on a system. In dealing with fluctuations, one can conceive of constructing an exceptionally rigid isolated system of constant volume V that contains a fixed number of moles n of material without change in composition. This is to be contrasted with intensive variables T or P , or with thermodynamic variables such as E or S that cannot be constrained, and therefore are expected to undergo fluctuations.

With V and n constant, let us set $x = \tilde{E}(T)$, $d\tilde{S} = (1/T)d\tilde{E}$, and set $(\partial^2 \tilde{S} / \partial \tilde{E}^2)_V = -(1/T^2)(\partial T / \partial \tilde{E})_V = -1/T^2 \tilde{C}_V$, where \tilde{C}_V is the molar heat capacity at constant volume and composition; for ideal gases, $\tilde{C}_V = 3R/2$. Thus, according to Eq. (1.17.24), fluctuations in energy are characterized by

$$\langle \Delta \tilde{E}^2 \rangle = RT^2 \tilde{C}_V. \quad (1.17.25)$$

Fluctuations in E incur fluctuations in T . For an ideal gas at constant V and n , we anticipate a later independent derivation: we introduce Eq. (2.4.5) to write $d\tilde{S} = \tilde{C}_V d \ln T$; whence for constant \tilde{C}_V , $(\partial^2 \tilde{S} / \partial T^2)_V = -\tilde{C}_V / T^2$, and

$$\langle \Delta T^2 \rangle = \frac{RT^2}{\tilde{C}_V}. \quad (1.17.26)$$

At constant V , n fluctuations in T also engender fluctuations in P . For an ideal gas, these are found via Eq. (2.4.7) as $d\tilde{S} = \tilde{C}_V d \ln P$, so that $(\partial^2 \tilde{S} / \partial P^2) = -P^2$. By Eq. (1.17.24),

$$\langle \Delta P^2 \rangle = \frac{RP^2}{\tilde{C}_V}. \quad (1.17.27)$$

Examination of the above relations shows that the fluctuations generally are very small for macroscopic systems.

Further Examples

The above examples apply to isolated systems in which volumes, mole numbers, and the equilibrium values of E (hence, of S) are constant. In many cases, one wishes to consider systems that interact with the surroundings, by exchanging heat or work or matter—the enlarged unit being isolated. As usual, we assume the reservoir to be so immense that fluctuations in its intensive variables— T_0 , P_0 , and μ_0 in the present case—remain absolutely miniscule compared to those anticipated for the system; i.e., T_0 , P_0 , and μ_0 are presumed to be fixed. Further, the total energy, volume, and mole numbers E_t , V_t , and n for the isolated compound unit at equilibrium are also assumed to be constant. Any changes in entropy are then subject to the requirement (unsubscripted variables refer to the system)

$$\begin{aligned} dS_t &= dS + dS_0 = dS + dE_0/T_0 + (P_0/T_0)dV_0 - (\mu_0/T_0)dn_0 \\ &= (1/T_0)(T_0dS - dE - P_0dV + \mu_0dn) \equiv -dL/T_0, \end{aligned} \quad (1.17.28a)$$

where we have introduced a new function of state,

$$L(x) = E - T_0S + P_0V - \mu_0n, \quad (1.17.28b)$$

which is termed¹ the *availability*. In the second line of Eq. (1.17.28a), we invoked overall conservation of energy, volume, and mole numbers. Clearly, the quantity, $-L/T_0$, is now to be used in place of S , so that Eq. (1.17.21) reads

$$f(x) \propto e^{-L(x)/RT_0}. \quad (1.17.29)$$

To prevent proliferation of symbols, for the remainder of this section, *all extensive variables are to be treated as molar quantities*; $n = 1$ in Eq. (1.17.28b).

To show how to use the above reformulation, consider fluctuations in volume dV of the system that arise when the rigid partition between system and surroundings is replaced by a flexible one. This in turn engenders fluctuations in T and P . With dE specified explicitly as usual at constant n , we then find from Eq. (1.17.28b) that (for the molar values)

$$dL = (T - T_0)dS + (P_0 - P)dV. \quad (1.17.30)$$

On the further assumption that the process under study is reversibly adiabatic (i.e., the flexible partition is impervious), a second differentiation of Eq. (1.17.30) yields $\partial^2 L / \partial V^2 = -(\partial P / \partial V)_S$, leading to

$$\langle \Delta V^2 \rangle = -RT_0(\partial V / \partial P)_S, \quad (1.17.31)$$

where the derivative is proportional to the adiabatic compressibility βV . On the other hand, if heat exchange is permitted under isochoric conditions, a double differentiation of Eq. (1.17.30) yields $\partial^2 L / \partial S^2 = (\partial T / \partial S)_V$, so that

$$\langle \Delta S^2 \rangle = R\tilde{C}_V T_0 / T \quad (1.17.32)$$

is the variance in the entropy fluctuations.

Correlated Fluctuations

One may proceed further: if E and V are both allowed to fluctuate at constant composition, we must expand L in a double Taylor series by analogy to Eq. (1.17.13), writing

$$L = L_e + (1/2)\alpha_{EE}\Delta E^2 + \alpha_{EV}\Delta E\Delta V + (1/2)\alpha_{VV}\Delta V^2. \quad (1.17.33)$$

From Eq. (1.17.28b), one obtains $(\partial L / \partial E)_V = 1 - T_0 / T$; $(\partial L / \partial V)_E = P_0 - T_0 P / T$, as is detailed in Appendix A2. A second differentiation leads to the coefficients called for in Eq. (1.17.33):

$$\alpha_{EE} \equiv (\partial^2 L / \partial E^2)_V = (T_0 / T^2)(\partial T / \partial E)_V = T_0 / C_V T^2 \quad (1.17.34a)$$

$$\alpha_{EV} \equiv (\partial^2 L / \partial E \partial V) = (T_0 / T^2)(\partial T / \partial V)_E = -T_0 [\partial(P/T) / \partial E]_V \quad (1.17.34b)$$

$$\alpha_{VV} \equiv (\partial^2 L / \partial V^2)_E = -T_0 [\partial(P/T) / \partial V]_E. \quad (1.17.34c)$$

As already implied, the above derivatives are evaluated in the limit of zero fluctuations, hence, are constants with respect to the integrations over ΔE or ΔV contemplated below.

As the next step, we write

$$f(E, V) \propto \exp\{-[\alpha_{EE}\Delta E^2 + 2\alpha_{EV}\Delta E\Delta V + \alpha_{VV}\Delta V^2] / 2RT\}, \quad (1.17.35a)$$

which may be readily recast in two equivalent forms:

$$f(E, V) \propto \exp\left\{-\alpha_{EE}[\Delta E + (\alpha_{EV} / \alpha_{EE})\Delta V]^2 / 2RT - (\alpha_{VV} - \alpha_{EV}^2 / \alpha_{EE})\Delta V^2 / 2RT\right\} \quad (1.17.35b)$$

$$f(E, V) \propto \exp\left\{-\alpha_{VV}[\Delta V + (\alpha_{EV} / \alpha_{VV})\Delta E]^2 / 2RT - (\alpha_{EE} - \alpha_{EV}^2 / \alpha_{VV})\Delta E^2 / 2RT\right\}. \quad (1.17.35c)$$

The fluctuations in E and V are then correlated, unless $\alpha_{EV} = 0$, as is the case for an ideal gas.

One is frequently interested in determining fluctuations in V or in E independently. This requires that one investigate the integrated forms $f(V) = \int f(E, V) d\Delta E$ or $f(E) = \int f(E, V) d\Delta V$. In integrating Eq. (1.17.35b) over ΔE , the quantity ΔV is an independent variable; the remaining multiplying quantities are also independent of the integration variable. Thus, the second exponential does not involve ΔE and may be moved as a constant factor outside the integral. The exponent of the first

factor is of a functional form such that one may set $d\Delta E = d\{\alpha_{EE}[\Delta E + (\alpha_{EV}/\alpha_{EE})\Delta V]\} \equiv dx$. Aside from the constant factor, the integral is then specified by $\int \exp(-x^2)dx$, which converges to a constant. This leaves

$$f(V) \propto \exp\left\{-\left(\alpha_{VV} - \alpha_{EV}^2/\alpha_{EE}\right)\Delta V^2/2RT\right\}, \quad (1.17.36)$$

which is of the desired Gaussian form. The determination of the terms in parentheses is detailed in Appendix A2: on setting $T = T_0$, one obtains $\alpha_{VV} - \alpha_{EV}^2/\alpha_{EE} = -(\partial P/\partial V)_T$, so that one recovers the T analog of Eq. (1.17.31). More generally,

$$\langle \Delta V^2 \rangle = -RT(\partial V/\partial P)_{T,n}. \quad (1.17.37)$$

Operations on Eq. (1.17.35c) involving $\langle \Delta E^2 \rangle$ are handled in a similar manner, as detailed in Appendix A3. The quantity of interest is given by

$$\alpha_{EE} - \frac{\alpha_{EV}^2}{\alpha_{VV}} = \frac{1}{C_V T} \left\{ \frac{(\partial P/\partial V)_T}{(\partial P/\partial V)_T - (T/C_V)(\partial E/\partial V)_T} \right\}. \quad (1.17.38)$$

For an ideal gas, the second term in the denominator vanishes; one then recovers the result (1.17.25); the above is its generalization to cases other than ideal gases.

Appendices

- A.1** Consider the relation $L_{11}X_1^2 + (L_{12} + L_{21})X_1X_2 + L_{22}X_2^2 \geq 0$. We investigate what are the necessary and sufficient conditions for the above sum to be nonnegative. For this purpose, introduce a change of variables; let $G \equiv 2L_{11}X_1 + (L_{12} + L_{21})X_1X_2$ and then eliminate X_1 ; this yields $\frac{G^2}{4L_{11}} + \left[L_{22} - \frac{(L_{12}+L_{21})^2}{4L_{11}}\right]X_2^2 \geq 0$. To satisfy this relation, it is sufficient to mandate that the multipliers of G^2 and of X_2^2 should be nonnegative. Thus, we first set $L_{11} \geq 0$; we then require that $4L_{22}L_{11} - (L_{12} + L_{21})^2 \geq 0$; and finally, that $L_{22} \geq 0$. With $L_{12} = L_{21}$, this verifies the assertions in Eq. (1.17.14).
- A.2** The details of the derivation depend on the use of Eqs. (1.3.6) and (1.3.8), Maxwell's equations, and on the chain rule of differentiation. We everywhere specialize to the case of constant composition, for which we set $S = S(E, V)$; $dS = (\partial S/\partial E)_V dE + (\partial S/\partial V)_E dV = (1/T)dE - [(\partial E/\partial V)_S/(\partial E/\partial S)_V]dV = (1/T)dE + (P/T)dV$. This yields the expression for $(\partial L/\partial V)_E$. From a second differentiation of $(\partial L/\partial E)_V$ and of $(\partial L/\partial V)_E$, we recover Eq. (1.17.34). Then $(\partial^2 L/\partial E \partial V) = + (T_0/T^2)(\partial T/\partial V)_E = - (T_0/T^2)(\partial E/\partial V)_T/(\partial E/\partial T)_V$, in which we now set $(\partial E/\partial V)_T = (\partial E/\partial V)_S + (\partial E/\partial S)_V(\partial S/\partial V)_T = -P + (\partial E/\partial S)_V(\partial S/\partial V)_T = -P + T(\partial P/\partial T)_V = T^2[\partial(P/T)/\partial T]_V$. We then find $(\partial^2 L/\partial E \partial V) = -T_0[(\partial(P/T)/\partial T)_V(\partial T/\partial E)_V] = -T_0[(\partial(P/T)/\partial E)_V]$. The last term may be expanded as $(T_0/C_V)[P/T^2 - (1/T)(\partial P/\partial T)_V]$. To obtain Eq. (1.17.37), we set $\alpha_{EV} = -T_0[(1/T)(\partial P/\partial E)_V - (P/T^2)(\partial T/\partial E)_V] = -T_0[(1/T)(\partial P/\partial T)_V(\partial T/\partial E)_V - (P/T^2 C_V)] = (T_0/C_V)[(P/T^2) - (1/T)(\partial P/\partial T)_V]$. Also, $\alpha_{VV} = -T_0\{[\partial(P/T)/\partial V]_T + [\partial(P/T)/\partial T]_V[\partial T/\partial V]_E\} = -T_0\{(1/T)(\partial P/\partial V)_T - (1/T)[(\partial P/\partial T)_V - P/T][\partial E/\partial V]_T [\partial E/\partial T]_V^{-1}\}$. Introduce the caloric equation of state to obtain

$\alpha_{VV} = -T_0\{(1/T)(\partial P/\partial V)_T - C_V^{-1}[(\partial P/\partial T)_V - P/T]^2\}$. Last, use Eq. (1.17.34c); straightforward algebra yields Eq. (1.17.37).

A.3 We begin with $\alpha_{EE} - \frac{\alpha_{EV}^2}{\alpha_{VV}} = \frac{T_0}{C_V T^2} + \frac{T_0(1/C_V^2)[\partial(P/T)/\partial T]_V^2}{[\partial(P/T)/\partial V]_T - (T^2/C_V)[\partial(P/T)/\partial T]_V^2}$, so that

$$\alpha_{EE} - \frac{\alpha_{EV}^2}{\alpha_{VV}} = \frac{T_0}{C_V T^2} \frac{[\partial(P/T)/\partial V]_T}{[\partial(P/T)/\partial V]_T - (T^2/C_V)[\partial(P/T)/\partial T]_V^2}. \text{ Set } T = T_0.$$

$$\alpha_{EE} - \frac{\alpha_{EV}^2}{\alpha_{VV}} = \frac{1}{C_V T} \frac{(\partial P/\partial V)_T}{(\partial P/\partial V)_T - (T/C_V)[T(\partial P/\partial T)_V - P]}. \text{ The factor in square brackets is equal}$$

to $(\partial E/\partial T)_V$. We thus recover Eq. (1.17.38).

Reference

- 1.17.1.** J.R. Waldram, *The Theory of Thermodynamics* (University Press, Cambridge, UK, 1985), Chapter 16.

Thermodynamic Properties of Ideal Systems

2

2.1 Equilibrium in a System of Several Components and Phases

With preliminaries out of the way we are ready to undertake a study of physical phenomena. We begin with the very severe restrictions placed on a system composed of several components distributed among a number of phases. The basic condition to be met requires that at equilibrium the Gibbs free energy be at a minimum, which condition will be realized below by requiring that the temperature, pressure, as well as the chemical potential of each component, be uniform throughout the system. Here we reintroduce the specialized meaning of components, as defined in Section 1.1. We also restrict ourselves to the performance of mechanical work; modifications required for additional types of work will be dealt with later. Lastly, we assume that every one of the c components is present in every phase; a derivation of the final results under the contrary condition is left as an exercise.

By way of introduction consider the chemical potentials for a two-phase, one-component system at fixed temperature and pressure, where $G = n'\mu' + n''\mu''$. The accents distinguish between the two phases, or more generally, between two regions of space. Suppose that at some instant $\mu' > \mu''$. The system can then not be at equilibrium: our earlier discussions showed that the chemical potential depends on the local concentrations of material; hence, distinct μ values correspond to different concentrations of the two constituents. Therefore, spontaneous processes set in that ultimately result in the equalization of chemical concentration in the two regions, and thus, in the equalization of μ' and μ'' . At constant T and P this can occur only by a transfer of matter from one phase or region to the other. Let a transfer of $-dn' = +dn'' > 0$ moles from phase $'$ to phase $''$ take place; the corresponding change in Gibbs free energy then is $dG = (\mu'' - \mu')dn$, where we set $dn \equiv dn''$. On assuming that $\mu' > \mu''$, we find that $dG < 0$; i.e., matter is transferred spontaneously from the phase of higher chemical potential to the phase of lower chemical potential. Hence, a difference in chemical potential represents a “driving force” for transfer of chemical species, rather analogous to the difference of electrical potential that is a “driving force” for electrically charged species. As in the case of an electrical potential, equilibrium is achieved only by an equality of the chemical potential for the species in question throughout the entire system. Just as the relative magnitudes of electrical potentials determine the direction of current flow between the two conductors, so the relative magnitudes of chemical potentials of a given component in two phases in contact determine the direction of transfer of the component between the phases. These statements will now be amplified by enlarging our discussion.

Our task consists in setting up criteria for establishing equilibrium conditions for a system of c components distributed among p phases, and in deriving the Gibbs phase rule. We start by writing the total Gibbs free energy for the combination of phases in the system as

$$G = G' + G'' + \dots + G^{(p)}, \quad (2.1.1)$$

in which $G', G'', \dots, G^{(p)}$ are the Gibbs free energies in phase 1, 2, ..., p . Each phase contains c distinct chemical species, enumerated by the index i . We neglect the interfacial free energies; if these are prominent the discussion of Sections 5.3 and 5.4 must be taken into account.

As shown in Section 1.9, when equilibrium prevails the Gibbs free energy for the entire system is at a minimum, with $\delta G = 0$; hence, we require that

$$\delta G = \delta G' + \delta G'' + \dots + \delta G^{(p)} = 0, \quad (2.1.2)$$

which, however, is minimally subject to the following restrictions:

$$\delta P = 0, \quad \delta T = 0, \quad \text{and} \quad \delta n_i = 0, \quad \text{all } i \quad (2.1.3)$$

where the n_i are the mole numbers of the species i in the entire composite system; these, along with T and P have been chosen as the independent variables.

The above relations must be compared to those that apply to the individual phases in isolation. For example, for phase 1, as identified by the prime superscript, we find

$$\delta G^{0'} = -S^{0'} \delta T^{0'} + V^{0'} \delta P^{0'} + \sum_{i=1}^c \mu^{0'} \delta n^{0'}. \quad (2.1.4)$$

The superscript 0 serves as a reminder that we deal with isolated phases, each at its own temperature T^0 , pressure P^0 , and with mole numbers n_i^0 that generally differ in each of the phases. We also take cognizance of the condition $\sum_i x_i^0 = 1$ imposed on the mole fractions. Thus, each of the equations typified by Eq. (2.1.4) involves $2 + c - 1 = c + 1$ independent variables. The total number of variables associated with the p isolated phases, involved in the sum $\delta G^{0'} + \delta G^{0''} + \dots + \delta G^{0(p)}$ is thus $p(c + 1)$.

We now combine all phases and allow thermal, mechanical, and chemical equilibrium to take place throughout the composite system. The temperatures T , pressures P , and mole numbers n_i now differ from those of the isolated phases. For the combined set of phases the equilibrium condition must be restated in the following manner:

$$\begin{aligned} \delta G = & -(S' \delta T' + S'' \delta T'' + \dots + S^{(p)} \delta T^{(p)}) \\ & + (V' \delta P' + V'' \delta P'' + \dots + V^{(p)} \delta P^{(p)}) \\ & + \left(\mu_1' \delta n_1' + \mu_1'' \delta n_1'' + \dots + \mu_1^{(p)} \delta n_1^{(p)} \right) \\ & + \left(\mu_2' \delta n_2' + \mu_2'' \delta n_2'' + \dots + \mu_2^{(p)} \delta n_2^{(p)} \right) \\ & + \dots + \\ & + \left(\mu_c' \delta n_c' + \mu_c'' \delta n_c'' + \dots + \mu_c^{(p)} \delta n_c^{(p)} \right) = 0. \end{aligned} \quad (2.1.5)$$

To ensure that the Gibbs free energy is actually at a minimum, i.e., that the sum in Eq. (2.1.5) should vanish, we introduce the following constraints: at equilibrium the temperature and pressure must be uniform throughout the system; we require that

$$T' = T'' = \dots = T^{(p)} \equiv T \quad \text{or} \quad \delta T' = \delta T'' = \dots = \delta T^{(p)} \equiv \delta T = 0 \quad (2.1.6a)$$

(2.1.6b)

On applying these conditions, the first two lines of Eq. (2.1.5) are found to vanish.

As a second step we impose the conservation of mole numbers for every component in the overall closed system:

(2.1.6c)

followed by an additional requirement, namely, that the chemical potential of each component be uniform throughout the system. Thus, we set

(2.1.7)

For, on imposing this set of requirements on Eq. (2.1.5) we do satisfy the conditions (2.1.6c): $\delta n_1 = \delta n_2 = \dots = \delta n_c = 0$, whereby the remaining lines in Eq. (2.1.5) now vanish. Thus, as required, δG does indeed vanish for the entire system at equilibrium.

We have now provided the necessary and sufficient conditions that characterize the equilibrium conditions among phases: *Aside from uniformity of temperature and pressure, the chemical potential μ_i for every one of the c components individually must be the same in each of the p phases.*

The number of degrees of freedom f for the assembly of phases may now be established: As stated earlier, $p(c + 1)$ independent variables are involved in the specification of the equilibrium state of all the separate phases. On combining these phases and reestablishing equilibrium we must take account of the $2(p - 1)$ constraints in Eqs. (2.1.6a and b) that ensure uniformity in T and P , and the $c(p - 1)$ interrelations in Eq. (2.1.7). The totality of constraints therefore is $(c + 2)(p - 1)$. The number of degrees of freedom remaining is then

(2.1.8)

Equation (2.1.8) represents the famous *phase rule of Gibbs* (1875–1878). Knowing the number of components and phases in a given system, and assuming that T and P for the system as a whole are uniformly variable, Eq. (2.1.8) indicates how many state variables may be independently adjusted over limited ranges without altering the number of phases of the system. The ramifications of the phase rule will be discussed below.

Exercises

2.1.1. How must the Gibbs phase rule be modified to take account of the following cases: (a) A multiphase system is placed between two charged parallel condenser plates? (b) One or more of the components are absent from one or more of the phases present? (c) Several distinct

regions of the system are maintained at different pressures by means of semipermeable membranes? Document your answers fully.

- 2.1.2.** How must the derivation of the Gibbs phase rule be modified if work other than mechanical P - V work is performed on or by the system? (Hint: classify these degrees of freedom with P and V and proceed with an expanded derivation.)
- 2.1.3.** What tacit assumption has been made in proceeding from Eq. (2.1.1) to Eq. (2.1.2)?

2.2 Achievement of Equilibrium

We consider here how to characterize the process whereby an isolated system achieves the equilibrium state, after setting out from a set of specified initial conditions. The ensuing discussion is preliminary, heuristic—in common parlance involves a lot of hand waving—that must be firmed up in Chapter 6. However, the discussion serves the purpose as an introductory treatment that is readily accessible.

The equilibration process is governed by corollaries of the first and second laws; in any process the energy in an isolated system must remain constant and the entropy cannot decrease. These requirements may not be sufficient to determine the final equilibrium state; additional experimental data and constraints may have to be inserted, as illustrated in the examples discussed below.

Characterization of Heat Flow

Consider the thermal equilibration of two systems, with rigid boundaries, initially at temperatures T' and T'' that are joined via an adiabatic partition, which is allowed to become slightly diathermic (See Figure 2.2.1). The resulting heat transfer is assumed to proceed with all deliberate speed; i.e., at a pace that permits us to assume that T' and T'' , while individually variable, remain uniform within the two compartments, except very close to the interfacial partition. So long as the compound system remains isolated, interfacial phenomena may be ignored, and the energies and entropies remain additive, we find that

$$E' + E'' = E_t \quad \text{or} \quad dE' + dE'' = 0, \quad (2.2.1)$$

and

$$S = S'(E', V') + S''(E'', V''). \quad (2.2.2)$$

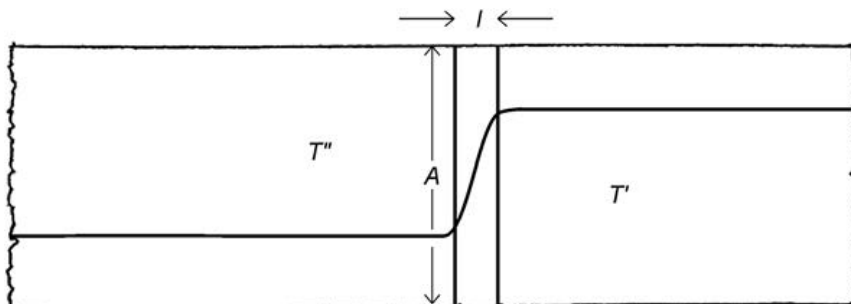


FIGURE 2.2.1

Temperature profile for the flow of heat between a region at temperature T' and a second region at temperature T'' , separated by a narrow transition region of cross section A and length l .

If the walls are rigid we also require $dV' = dV'' = 0$. In an infinitesimal exchange of heat between the two subsystems, the above relation reads

$$dS = (\partial S'/\partial E')_{V'} + (\partial S''/\partial E'')_{V''} \geq 0. \quad (2.2.3)$$

On account of Eq. (2.2.1) and the relation $(\partial E/\partial S)_V = T$, which holds under the assumed deliberate speed principle, Eq. (2.2.3) is changed to

$$dS = (1/T' - 1/T'')dE' \geq 0. \quad (2.2.4)$$

This immediately establishes the requirement $T' = T''$ as a necessary condition for thermal equilibrium, which is hardly news. Also, as the system approaches its equilibrium state the entropy approaches its final maximum value—we knew that already.

It is instructive to differentiate the above relation with respect to time t . We obtain

$$\dot{S} = (1/T' - 1/T'')(dE'/dt) \geq 0. \quad (2.2.5a)$$

Here $\dot{S} \equiv dS/dt$ represents the rate of entropy production during the energy transfer; this quantity cannot be negative and vanishes at equilibrium. Accordingly, the factors $(1/T' - 1/T'')$ and (dE'/dt) must be both positive or both negative. In the first case $T' < T''$ and $(dE'/dt) > 0$, i.e., the energy of the ' phase increases with time. Since no work has been performed it is reasonable to equate dE'/dt with the rate of heat transfer, \dot{Q} , across the internal boundary into the ' phase, in response to the postulated temperature difference. We thus rewrite Eq. (2.2.5a) in the form $\dot{S} = \Delta(1/T)\dot{Q}$ and define a *heat flux* by the relation $J_Q = \dot{Q}/A$, where A is the cross-sectional area of the diathermic partition. Since the changeover from T' to T'' takes place only over a small distance l perpendicular to the partition (see Figure 2.2.1) the product Al roughly defines a volume V over which the temperature changes occur. We may then write $\dot{S} = \Delta(1/T)VJ_Q/l$. In the limit of tiny l the ratio $\Delta(1/T)/l$ becomes the gradient $\nabla(1/T)$; also, $\dot{S}/V \equiv \dot{\theta}$ is the rate of entropy production per unit volume, which, as will be seen in Chapter 6, is a quantity of great theoretical interest. Equation (2.2.5a) has thereby been rewritten in the more fundamental form

$$\dot{\theta} = \nabla(1/T)J_Q \geq 0. \quad (2.2.5b)$$

The preceding chain of reasoning is obviously very crude; for a proper derivation of Eq. (2.2.5b) the reader is referred to Section 6.1. We can nevertheless obtain several interesting insights without the benefit of the full machinery of irreversible thermodynamics. Note that Eq. (2.2.5b) involves the product of a *flux* J_Q and of a generalized (thermal) *force* or *affinity* $\nabla(1/T) \equiv F_T$ that drives the heat flow. The two act in such a manner that heat always flows from the hotter to the colder body. This again is not exactly news, but at least shows the consistency of the entire approach.¹ When $\dot{\theta} = 0$ equilibrium prevails; J_Q and F_T both vanish.

The dependence of J_Q on F_T cannot be determined from classical thermodynamics alone; rather, one must invoke microscopic transport theory for this purpose. Nevertheless, on general principles one may assert that sufficiently close to equilibrium the flux should vary linearly with the applied force according to

$$J_Q = L_T F_T, \quad (2.2.6a)$$

where L_T is a parametric function, independent of J_Q or F_T , known as the *phenomenological coefficient*. We then write

$$J_Q = L_T \nabla(1/T) = -(L_T/T^2) \nabla T \equiv -\kappa \nabla T, \quad (2.2.6b)$$

where $\kappa \equiv L_T/T^2$ is called the *thermal conductivity*; Eq. (2.2.6b) is a formulation of *Fourier's law of heat conduction*. Accordingly, we can set

$$\dot{\theta} = L_T F_t^2 = J_Q^2/L_T. \quad (2.2.7)$$

Then, according to Eqs. (2.2.6b) and (2.2.7), we require that $L_T \geq 0$ and $\kappa \geq 0$, in order that $\dot{\theta}$ remain nonnegative.

System with Energy Transfer at Variable Volume

We now extend the above discussion by examining an isolated compound system with a fixed total volume, containing a sliding partition that is initially locked, and that provides for adiabatic insulation of two compartments at pressures P' and P'' , temperatures T' and T'' , and individual volumes V' and V'' . The system is allowed to relax after slowly releasing the lock and slowly rendering the partition slightly diathermic (again, the deliberate speed principle). Entropy changes in both compartments now occur in accord with the relation $dS = T^{-1}[dE + PdV]$, no other forms of work being allowed. The constraints are $dV' + dV'' = 0$, (rather than $dV' = dV'' = 0$, as before) and $dE' + dE'' = 0$. By the procedure adopted earlier the entropy depends on the individual energies and volumes, so that

$$dS = (\partial S'/\partial E')_{V'} dE' + (\partial S''/\partial E'')_{V''} dE'' + (\partial S'/\partial V')_{E'} dV' + (\partial S''/\partial V'')_{E''} dV'' \geq 0. \quad (2.2.8)$$

With $dS = T^{-1}[dE + PdV]$ one obtains $(\partial S/\partial E)_V = 1/T$ and $(\partial S/\partial V)_E = P/T$; whereby Eq. (2.2.8) becomes

$$dS = (1/T')_{V'} dE' + (1/T'')_{V''} dE'' + (P'/T')_{E'} dV' + (P''/T'')_{E''} dV'' \geq 0. \quad (2.2.9)$$

Finally, with $dE'' = -dE'$ and $dV'' = -dV'$ for the totally isolated system one obtains

$$\dot{S} = (1/T' - 1/T'')(dE'/dt) + (P'/T' - P''/T'')(dV'/dt) \geq 0. \quad (2.2.10)$$

This expression, in conjunction with the arguments that led to Eq. (2.2.5b), suggests that we introduce the *fluxes* $J_E \equiv dE'/Adt$ and $J_W \equiv dV'/Adt$, and that we convert $\Delta(1/T) = 1/T' - 1/T''$ and $\Delta(P/T) = P'/T' - P''/T''$ into *affinities*, such that for small l , $F_T = \Delta(1/T)/l \equiv \nabla(1/T)$ and $F_P = \Delta(P/T)/l \equiv \nabla(P/T)$. In the absence of any other processes J_W is to be construed as a work flux; then J_E may be regarded as a heat flux. We further introduce the rate of entropy production per unit volume in the manner discussed above to obtain

$$\dot{\theta} = \nabla(1/T)J_E + \nabla(P/T)J_W, \quad (2.2.11)$$

which identifies $\nabla(1/T)$ and J_E as well as $\nabla(P/T)$ and J_W as two *conjugate flux-force variables*. Equilibrium is then characterized by the necessary condition $F_T = F_P = 0$, which leads to the requirements that $T' = T''$ and $P' = P''$ as equilibrium constraints. Again, this is consistent with well-established principles.

We now introduce a very important new principle, based on Eq. (2.2.11): we postulate a linear dependence of the fluxes on the forces, such that both forces combine to drive both fluxes. The resulting relations

$$\begin{aligned} J_E &= L_{11}F_T + L_{12}F_P \\ J_W &= L_{21}F_T + L_{22}F_P, \end{aligned} \quad (2.2.12)$$

are known as *phenomenological equations*, and the various L are known as *phenomenological coefficients*. Clearly, Eq. (2.2.12) displays interference effects, in that the driving force for heat flow (or for work performance) also affects the work (or energy) flux. These matters are taken up in much further detail in Chapter 6. For now we only note that the rate of entropy production is specified by

$$\dot{\theta} = F_T J_E + F_P J_W = L_{11} F_T^2 + (L_{12} + L_{21}) F_P F_T + L_{22} F_P^2 \geq 0. \quad (2.2.13)$$

In order to render $\dot{\theta}$ nonnegative it is necessary and sufficient to require that

$$L_{11} \geq 0; \quad 4L_{11}L_{22} - (L_{12} + L_{21})^2 \geq 0; \quad L_{22} \geq 0, \quad (2.2.14)$$

for which a derivation is furnished below. This indicates that the “diagonal” coefficients in Eq. (2.2.12) must remain nonnegative, while the off-diagonal coefficients must satisfy stringent requirements.

Transfer of Energy and Matter

We next examine the case of two subsystems separated by a rigid partition that is rendered diathermic and rendered permeable to one species present in different amounts in two compartments held at different temperatures. By an extension of earlier reasoning we invoke the relation $dS = T^{-1}[dE - \mu dn]$ to write

$$\dot{S} = (1/T' - 1/T'')(dE'/dt) + (\mu''/T'' - \mu'/T')(dn'/dt) \geq 0, \quad (2.2.15)$$

from which it follows that at equilibrium

$$T' = T'' \quad \text{and} \quad \mu' = \mu'', \quad (2.2.16)$$

in consonance with earlier findings. According to Eq. (2.2.15) we can further generate a set of fluxes $J_E \equiv dE/Adt$ and $J_n \equiv dn'/Adt$, involving the flow of heat and of chemical species, respectively, and the corresponding generalized forces $F_T \equiv \nabla(1/T)$ and $F_n \equiv \nabla(\mu/T)$. One then sets up linear phenomenological equations of the form, analogous to Eq. (2.2.12),

$$\begin{aligned} J_E &= L_{33} F_T + L_{34} F_n \\ J_n &= L_{43} F_T + L_{44} F_n. \end{aligned} \quad (2.2.17)$$

The rate of entropy production is specified by

$$\dot{\theta} = F_T J_E + F_n J_n = L_{33} F_T^2 + (L_{34} + L_{43}) F_n F_T + L_{44} F_n^2 \geq 0. \quad (2.2.18)$$

together with the requirements

$$L_{33} \geq 0; \quad 4L_{33}L_{44} - (L_{34} + L_{43})^2 \geq 0; \quad L_{44} \geq 0. \quad (2.2.19)$$

The generalization to the case of a sliding partition is to be handled as an exercise.²

Inequalities that Guarantee a Nonnegative Rate of Entropy Production

We consider here the necessary and sufficient conditions that guarantee that Eq. (2.2.18) remains nonnegative. For this purpose introduce the change of variable

$$G \equiv 2L_{33}F_T + (L_{34} + L_{43})F_n \quad (2.2.20)$$

and eliminate F_T from Eq. (2.2.18). This yields the relation

$$(1/4L_{33})G^2 + \left[L_{44} - (L_{34} + L_{43})^2/4L_{33} \right] F_n^2 \geq 0. \quad (2.2.21)$$

Clearly, the multipliers of G^2 and F_n^2 must remain nonnegative to satisfy Eq. (2.2.21). Thus, we first set $L_{33} \geq 0$, then require that $L_{44} - (L_{34} + L_{43})^2/4L_{33} \geq 0$, and finally note that we are forced to set $L_{44} \geq 0$. This establishes Eq. (2.2.19).

Comment and Exercise

- 2.2.1.** The above derivation shows that the zeroth law of Thermodynamics, as commonly introduced in elementary treatments, which states that heat flows spontaneously from a hotter to a colder region, really should not be considered a fundamental pronouncement.
- 2.2.2.** Generalize the above derivations so as to handle the case of two subsystems at different temperatures, pressures, and mole numbers of a gas, separated by a moveable partition that is permeable to the gaseous species.

2.3 System of One Component and Several Phases; the Clausius–Clapeyron Equation

We begin here with a study of the application of the Gibbs phase rule, whereby we gain an understanding of elementary phase diagrams and their ramifications. For definiteness we take water under ordinary conditions as an example. For this one-component system the degrees of freedom are given by $f = 2, 1, 0$ when one, two, or three phases are present. In the liquid state the two available degrees of freedom are temperature and pressure; these may be varied independently over a considerable range without changing the state of aggregation of the liquid phase. By contrast, if one wishes to create conditions where water and steam coexist, T and P are no longer independently adjustable; the pressure is now determined by the temperature, or vice versa—only one degree of freedom is left. Thus, if at fixed $T < 647.2$ K the prevailing equilibrium pressure were raised (for example, by application of pressure through a piston) steam would continually condense, at close to the equilibrium pressure until only water is present (when the piston rests on the liquid level). The heat of condensation must be continually withdrawn, so as to maintain the temperature at a fixed value. The pressure on the water will then rise, as the piston continues to be forced against the liquid. Conversely, if the equilibrium pressure is reduced (by withdrawal of the piston) water would continue to evaporate, so long as the temperature of the liquid is maintained by supplying the heat of vaporization from external sources. On completion of the vaporization, only steam remains in the system. On the other hand, the process of raising the temperature of the water in a closed system raises the vapor pressure; the equilibrium values are tabulated in steam tables.

Under conditions where ice, water, and steam coexist no degree of freedom is left; this state can only be realized if the system is maintained at the so-called *triple point* $T = 273.16$ K and at $P = 4.58$ bar. For this reason the triple point of water serves as a convenient thermometric reference standard, as already mentioned in Section 1.2.

Representative Phase Diagram

A pictorial cartoon of the above discussion is provided in Figure 2.3.1 (the actual phase diagram for water looks rather different; see, e.g., Ref. 1, below), as a plot of T vs P . The three curves delineate

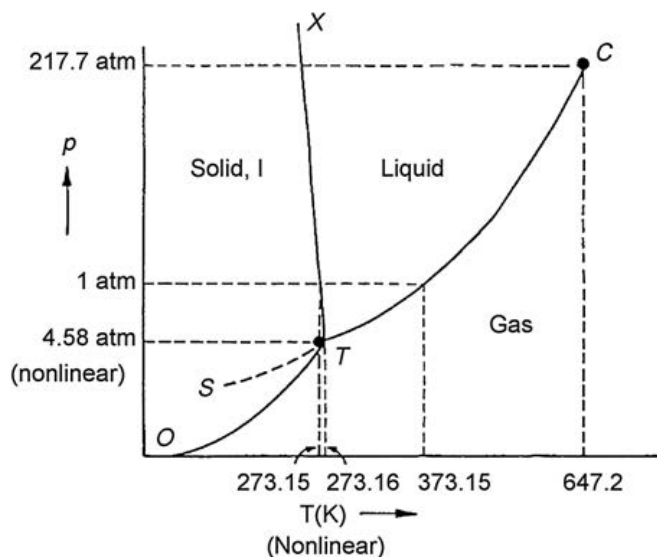


FIGURE 2.3.1

Sketch of the phase diagram of water (not drawn to scale).

three distinct regions within which pressure and temperature may be varied independently within limits, corresponding to the presence of only one phase. By contrast, the curves indicate the conditions under which two phases can coexist; they are the loci of experimental (T, P) values compatible with the presence of two phases. In other words, they indicate the dependence of T on P , or vice versa. Thus, to have ice and steam coexist one must adjust T and P to fall somewhere on the curve OT , and similarly for the other branches. T in the diagram represents the triple point, discussed earlier, and C , the critical point ($T = 647.2$ K, $P = 217.7$ bar), beyond which water and steam are indistinguishable. The description of critical phenomena will be taken up in detail in Chapter 7.

The transformation between water and steam can be depicted in the manner shown in Figure 2.3.2, which represents a plot of P vs the molar volume \tilde{V} at various temperatures close to the critical point. The shaded region indicates an excluded domain: for example, at $P = 15.3$ bar and $T = 473.2$ K water with molar volume \tilde{V}_a coexists with steam whose molar volume is \tilde{V}_b . No intermediate molar volumes characteristic of a single phase can exist under these conditions. As the pressure is raised beyond 15.3 bar at 473.2 K steam gas at molar volume \tilde{V}_b condenses to form liquid at molar volume \tilde{V}_a . The diagram also shows that as the temperature is raised the two volumes approach each other and ultimately coalesce at 647.2 K to a common value \tilde{V}_c . Above that temperature the two phases merge into one fluid phase.

So far we have simply described the curves in the phase diagram of Figure 2.3.1 as loci of conditions under which two phases coexist. We next provide the analytical relations to characterize such curves.

The Clausius–Clapeyron Equation

The derivation is based on the fact that when two phases A and B are in equilibrium their chemical potentials, μ_A and μ_B , must be equal, so that $d\mu_A = d\mu_B$; also, the pressure and temperature must be uniformly the same. On introducing Eq. (1.12.1d) one finds that

$$-\tilde{S}_A dT + \tilde{V}_A dP = -\tilde{S}_B dT + \tilde{V}_B dP, \quad (2.3.1)$$

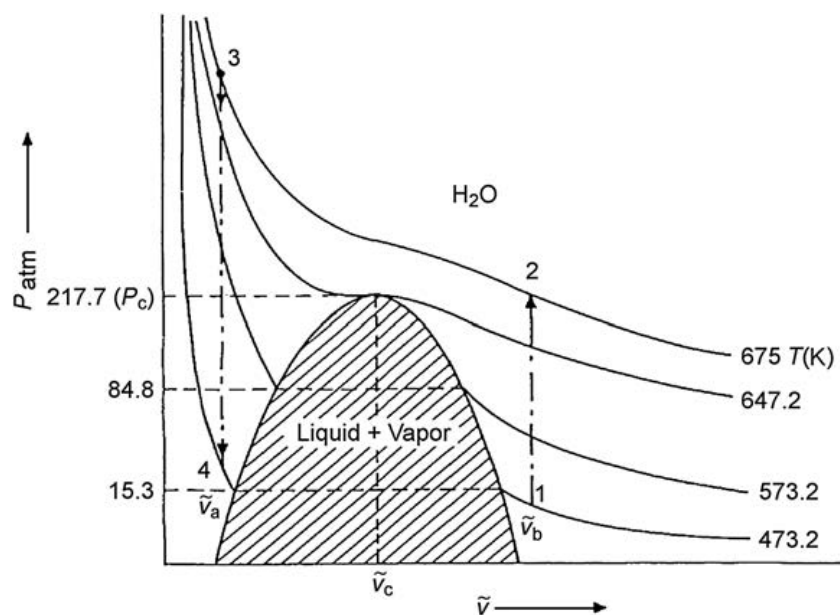


FIGURE 2.3.2

Pressure–volume relation for water in the vicinity of its critical point.

which may be rewritten in the form

$$(dP/dT) = (\tilde{S}_B - \tilde{S}_A) / (\tilde{V}_B - \tilde{V}_A). \quad (2.3.2)$$

This expression is known as the *Clausius–Clapeyron equation*. It is of historic significance, as representing a very early derivation that links different variables in an unsuspected manner—an example of the power of thermodynamic theory that served as a guideline for later theoretical developments.

The above relation shows up in many different guises. At equilibrium we may set $\mu_B - \mu_A = 0 = \tilde{H}_B - \tilde{H}_A - T(\tilde{S}_B - \tilde{S}_A)$, whence we find

$$(dP/dT) = (\tilde{H}_B - \tilde{H}_A) / T(\tilde{V}_B - \tilde{V}_A), \quad (2.3.3)$$

where T is the coexistence temperature for the two phases.

The above is often approximated in different ways. For example, when dealing with liquid–gas equilibria one frequently introduces the approximations $\tilde{V}_l \ll \tilde{V}_g$ and $\tilde{V}_g = RT/P$, which apply well below the critical point, but at temperatures sufficiently high for the perfect gas approximation to hold. On defining $\tilde{L}_v \equiv \tilde{H}_g - \tilde{H}_l$ as the molar latent heat of vaporization of the liquid Eq. (2.3.3) assumes the approximate form

$$(dP/dT) = \tilde{L}_v P / RT^2, \quad (2.3.4)$$

which may be recast as

$$(d \ln P / dT) = \tilde{L}_v / RT^2. \quad (2.3.5)$$

One should note that the Clausius–Clapeyron equation is sometimes used in reverse. Instead of employing temperature to control the equilibrium vapor pressure, experimentalists adjust the vapor pressure of a helium bath to control its temperature in the range 0.3–4.2 K, where the vapor pressures fall in a conveniently manageable range.

By way of contrast to Figure 2.3.1 we briefly consider a phase diagram that is more appropriate to CO_2 , shown in Figure 2.3.3. Here the solid–liquid coexistence curve has a positive slope, as contrasted

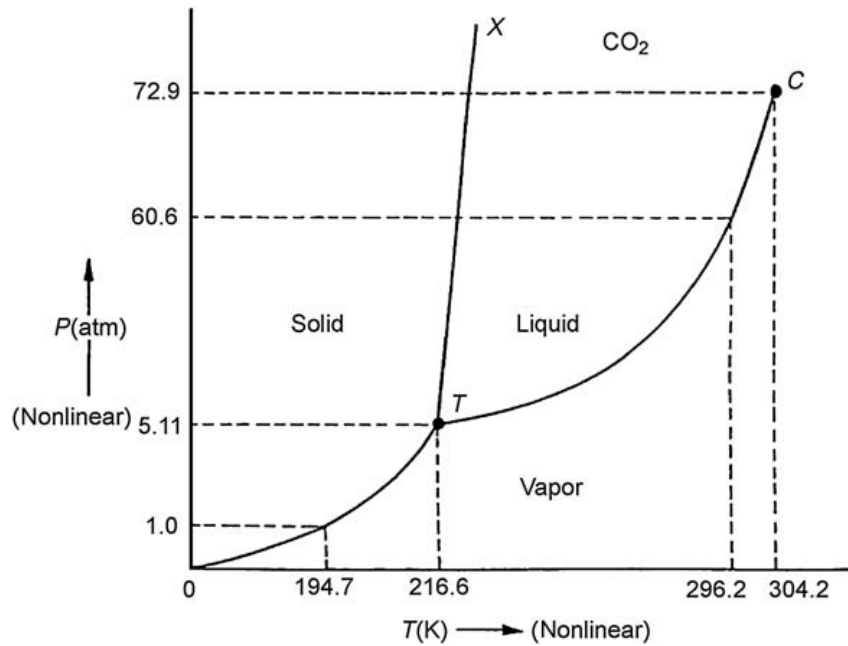


FIGURE 2.3.3

Sketch of the phase diagram for carbon dioxide (not drawn to scale).

with the case of water, where the slope is negative. This reflects the unusual case for H_2O for which $\tilde{V}_l < \tilde{V}_s$, corresponding to the teleological case of ice floating on top of water. In many other substances the reverse inequality holds, as in Figure 2.3.3. Also, in the case of CO_2 the triple point is located close to 5.11 bar. Hence, under ordinary conditions, solid CO_2 does not melt but vaporizes directly, a process frequently referred to as *sublimation*.

The van der Waals Equation of State

P - V curves of the type shown in Figure 2.3.2 are very common and are well simulated by the *van der Waals equation of state* for n moles of fluid

$$P = nRT/(V - nb) - an^2/V^2, \quad (2.3.6)$$

for which the variation of pressure with volume is sketched² for a series of temperatures in Figure 2.3.4. The parameters a and b must be determined by experiment. The dashed curve indicates an exclusion region that corresponds to the hatched region in Figure 2.3.2. Many other equations of state lead to very similar results, but the van der Waals equation of state is adopted frequently in the theoretical characterization of properties of fluids. We therefore examine its properties in further detail.

Clearly, a curve located between T_8 and T_9 in Figure 2.3.4 corresponds to the isotherm at the critical point, where its first and second derivatives vanish, as shown for water by the curve for 647.2 K in Figure 2.3.1. On imposing the requirements $(\partial P/\partial V)_T = (\partial^2 P/\partial V^2)_T = 0$ one finds that

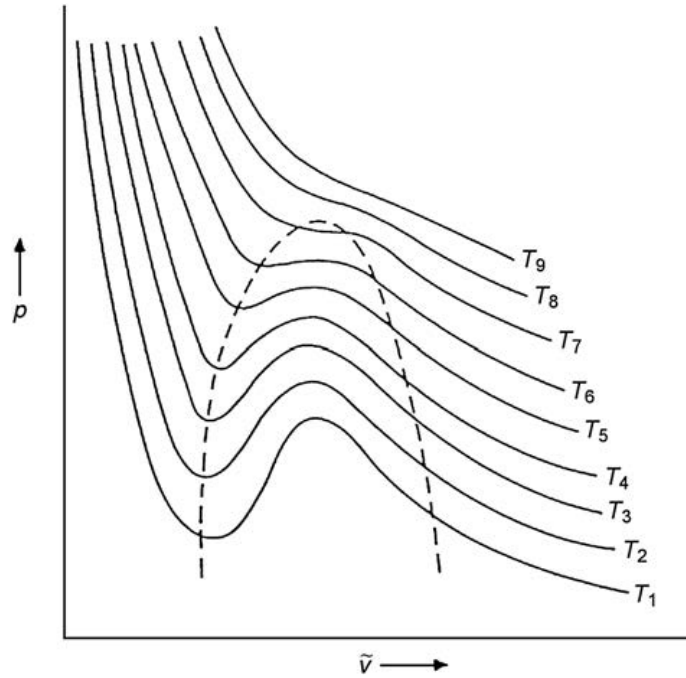


FIGURE 2.3.4

Schematic presentation of pressure–volume variations generated by the van der Waals equation of state.

$$-2a/\tilde{V}_c^3 + RT_c/(\tilde{V}_c - b)^2 = 0 \quad (2.3.7)$$

$$-3a/\tilde{V}_c^4 + RT_c/(\tilde{V}_c - b)^3 = 0. \quad (2.3.8)$$

Division of (2.3.7) by (2.3.8) leads to the relation

$$\tilde{V}_c = 3b. \quad (2.3.9)$$

When this is inserted in Eq. (2.3.7) one obtains

$$T_c = 8a/27bR. \quad (2.3.10)$$

Substitution of Eqs. (2.3.9) and (2.3.10) in the van der Waals equation of state leads to

$$P_c = a/27b^2. \quad (2.3.11)$$

Then the ratio

$$RT_c/P_c\tilde{V}_c = 8/3 \quad (2.3.12)$$

is a universal constant, whereas the individual critical constants do depend on the parameters a and b . Moreover, it is easy to show that on introducing the reduced variables $P_r \equiv P/P_c$, $V_r \equiv V/V_c$, $T_r \equiv T/T_c$ the van der Waals equation of state may be rewritten in the universal form

$$(P_r + 3/V_r^2)(V_r - 1/3) = 8T_r/3, \quad (2.3.13)$$

which is a very elegant formulation, since it involves solely the critical constants of fluids. Equation (2.3.13) is one example of the so-called *Law of Corresponding States*; to the degree to which

Eq. (2.3.13) is applicable, the relevant data for all fluids should fall on a single curve that illustrates the universality of some physical properties of materials. The extent to which this is the case is illustrated by an example in Chapter 7. Actually, the universality implied in Eqs. (2.3.12) and (2.3.13) is not well satisfied experimentally near the critical point. For, as shown in Chapter 7, the van der Waals equation of state does not reproduce the critical characteristics of fluids satisfactorily. Other commonly used equations of state suffer from similar defects. As will be shown, a different approach must be employed to characterize fluids near criticality.

Reference and Footnote

2.3.1. See, e.g., I. N. Levine, *Physical Chemistry*, 5th Ed., (McGraw Hill Boston, 2002), p. 209.

2.3.2. This is a distorted version of the experimental curves, to facilitate the depiction of the critical point.

2.4 Properties of Ideal Gases

Functions of State for an Ideal Gas

We now apply the basic thermodynamic principles to study physical properties of selected materials, the first of which is an ideal gas that obeys the equation of state $P\tilde{V} = RT$. For a mixture of ideal gases the individual chemical constituents i obey the relation $P_i V = n_i RT$, or $P_i \tilde{V} = RT$. As stated in Section 1.13, no material with such properties actually exists, but the ideal gas concept serves as a good model for many gases at a sufficiently high temperature and low pressure. On account of the simple equation of state it is worthwhile to examine the thermodynamic characteristics of this postulated species.

The Energy and Enthalpy of an Ideal Gas

To begin with, insert the equation of state for the ideal gas into the caloric equation of state, Eq. (1.12.7b), whence it is found that $(\partial E/\partial V)_T = 0$. This is a *second criterion* concerning ideal gases: their energy depends solely on temperature; thus, the differential energy assumes the abbreviated form $dE = (\partial E/\partial T)_V dT$. Then, on introducing the definition for the heat capacity, we find that

$$d\tilde{E} = \tilde{C}_V dT. \quad (2.4.1a)$$

Moreover, for ideal gases,

$$(\partial C_V/\partial V)_T = [(\partial/\partial V)(\partial E/\partial T)_V]_T = [(\partial/\partial T)(\partial E/\partial V)_T]_V = 0, \quad (2.4.1b)$$

which shows that at constant composition C_V likewise can at most depend on T . We next appeal to theory, Section 1.12, or to experiment: at sufficiently high temperatures and low pressures the molar heat capacity of a gas approximates ideal behavior $\tilde{C}_V = 3R/2$, a constant. This is no longer true of any actual gas at lower temperatures, closer to its liquefaction, as discussed in conjunction with the corollary of the third law. As a *third criterion* of an ideal gas we therefore require that C_V be a constant. Integration of (2.4.1a) then leads to the result

$$\tilde{E} = \tilde{C}_V T + \tilde{E}_0, \quad (2.4.2)$$

where the constant \tilde{E}_0 represents the molar energy of an ideal gas if it could be maintained down to $T = 0$. This choice for \tilde{E}_0 is obviously unrealistic, but immaterial, since energy can only be specified to within a completely arbitrary constant; only energy differences are unique.

By noting that $(\partial E / \partial V)_T = 0$ one finds that

$$\tilde{C}_P - \tilde{C}_V = R. \quad (2.4.3)$$

Accordingly, the molar enthalpy of the ideal gas becomes

$$\tilde{H} = \tilde{E} + P\tilde{V} = \tilde{E} + RT = (\tilde{C}_V + R)T + \tilde{E}_0 = \tilde{C}_P T + \tilde{E}_0. \quad (2.4.4)$$

It is readily shown (Ex. 1) that $(\partial C_P / \partial P)_T = 0$.

The Entropy of an Ideal Gas

The molar entropy of an ideal gas is another quantity of considerable interest. For reversible changes we note that

$$d\tilde{S} = T^{-1}(d\tilde{E} + Pd\tilde{V}) = (\tilde{C}_V/T)dT + (R/\tilde{V})d\tilde{V} = \tilde{C}_V d \ln T + R d \ln \tilde{V}. \quad (2.4.5)$$

On setting $Pd\tilde{V} + \tilde{V}dP = RdT$ and substituting for $Pd\tilde{V}$ we obtain the equivalent relation

$$d\tilde{S} = (\tilde{C}_V/T + R/T)dT - (R/P)dP = \tilde{C}_P d \ln T - R d \ln P. \quad (2.4.6)$$

Lastly, introducing $d \ln T = d \ln P + d \ln \tilde{V}$ into either of the above expressions yields

$$d\tilde{S} = \tilde{C}_V d \ln P + \tilde{C}_P d \ln \tilde{V}. \quad (2.4.7)$$

We have thus obtained three equivalent formulations for the differential entropy of an ideal gas. We may integrate between two specific limits; selecting Eq. (2.4.6) as an example we obtain

$$\int_{\tilde{S}_i}^{\tilde{S}_f} d\tilde{S} = \int_{T_i}^{T_f} \tilde{C}_P d \ln T - R \int_{P_i}^{P_f} d \ln P. \quad (2.4.8)$$

Assuming constant \tilde{C}_P we find

$$\tilde{S}_f = \tilde{S}_i + \tilde{C}_P \ln(T_f/T_i) - R \ln(P_f/P_i). \quad (2.4.9)$$

Let us now choose T_i and P_i as fixed reference values designated as T^* and P^* , and let T_f and P_f assume any arbitrary value; also, set $\tilde{S}(T^*, P^*) \equiv \tilde{S}^*$. Then the above expression assumes the form

$$\tilde{S} = \tilde{S}^* + \tilde{C}_P \ln(T/T^*) - R \ln(P/P^*). \quad (2.4.10a)$$

It is conventional to set $T^* = 273.15 \text{ K}$ and $P^* = 1 \text{ bar}$ as the standard states, but any other convenient values are just as acceptable, since changes in the above T^* and P^* values bring about compensating changes in $\tilde{S}^* = -\tilde{C}_P \ln T^* + R \ln P^*$.

Particularly in the earlier literature one also encounters the following formulation:

$$\tilde{S} = \tilde{S}^* + \tilde{C}_P \ln T - R \ln P, \quad (2.4.10b)$$

where we seem to run into a problem of dimensional analysis since the logarithmic arguments are not pure numbers; however, this difficulty is only apparent. For, in Eq. (2.4.10b) the reference entropy is now specified by $\tilde{S}^* = \tilde{S}_i - \tilde{C}_P \ln T_i + R \ln P_i$. Hence, if the units selected for P or T are altered in Eq. (2.4.10b) there also occurs an exactly compensating change in $\tilde{S} - \tilde{S}^*$. Thus, the value of \tilde{S} relative to \tilde{S}^* remains unaffected by the choice of units. However, the numerical values of \tilde{S} and \tilde{S}^* obviously do depend on the energy unit chosen for \tilde{C}_P and for R . Incidentally, on setting $T = T^*$ and $P^* = 1$ bar it does appear as though Eq. (2.4.10b) were afflicted with dimensional problems; so, it is best always to carry the P^* symbol along. Actually, statistical mechanics furnishes a relation for \tilde{S}^* , which is cited as the Sackur–Tetrode equation in Section 1.12.

Equation (2.4.10a) also shows that \tilde{S}^* represents the molar entropy of the ideal gas when the final and initial temperatures, as well as the final and initial pressures in the experiment are identical. However, the theoretical development fails to specify what such an initial condition should be. This indeterminacy allows one to justify the convention that is cited above for the *standard state* for the ideal gas: at whatever temperature prevails in a given experiment, *the standard state of an ideal gas is set at a pressure $P = 1$ bar*.

We deal in an analogous fashion with the equivalent forms for the entropy of the ideal gas:

$$\tilde{S} = \tilde{S}^{*'} + \tilde{C}_V \ln(T/T^*) + R \ln(\tilde{V}/\tilde{V}^*) \quad (2.4.11a)$$

$$\tilde{S} = \tilde{S}^{*''} + \tilde{C}_V \ln(P/P^*) + \tilde{C}_P \ln(\tilde{V}/\tilde{V}^*). \quad (2.4.11b)$$

The Gibbs Free Energy of an Ideal Gas

The Gibbs free energy for a particular ideal gaseous species is found by adopting Eq. (2.4.10b):

$$\begin{aligned} \tilde{G}(T, P) &= \tilde{H} - T\tilde{S} = \tilde{C}_P T + \tilde{E}_0 - T(\tilde{C}_P \ln T - R \ln P + \tilde{S}^*) \\ &= \tilde{G}^*(T, 1) + RT \ln P, \end{aligned} \quad (2.4.12a)$$

wherein

$$\tilde{G}^*(T, 1) \equiv \tilde{E}_0 + \tilde{C}_P(T - T \ln T) - T\tilde{S}^*(T, 1) \quad (2.4.12b)$$

represents the *standard value* of the molar Gibbs free energy of the ideal gas at a pressure of $P = 1$ bar at the prevailing temperature T . Equation (2.4.12a) reduces to an identity for $P = 1$ bar; also, $\tilde{G}(T, P)$ is identical with the chemical potential $\mu(T, P)$ of the ideal gas. Methods for determining μ are provided by statistical mechanics (Sections 1.12 and Chapter 10); experimental determinations are cited later.

We next generalize to a mixture of different ideal gases, for which the above expression applies to one component i in the mixture of ideal gases. In principle, for reversible changes we could simply replace \tilde{G} by μ_i and P , by P_i . However, the relation to be established is so important that we proceed by a different route: Entry [3], Table 1.12.I, as applied to the present case, reads $(\partial G/\partial P)_T = V = \sum_j n_j RT/P$. On partial differentiation with respect to n_i we obtain

$$(\partial \mu_i / \partial P)_T = \bar{V}_i = RT/P = (\partial \mu_i / \partial P_i)_T (\partial P_i / \partial P)_T, \quad (2.4.13a)$$

where P_i is the partial pressure of component i , which is related to the total pressure P by the mole fraction x_i : $P_i = x_i P$. Using the last equality we thus obtain

$$(\partial \mu_i / \partial P_i)_T = RT/P_i, \quad (2.4.13b)$$

which may be integrated between the limits P_i^0 and P_i at constant T to yield

$$\mu_i(T, P_i) = \mu_i(T, P_i^0) + RT \ln(P_i/P_i^0), \quad (2.4.14)$$

By convention we select for P_i^0 the *standard value of 1 bar*; then $\mu_i(T, 1) \equiv \mu_i^{OP}(T)$ is the standard chemical potential for component i of the ideal gas mixture. Thus, we obtain the final formulation

$$\mu_i(T, P_i) = \mu_i^{OP}(T) + RT \ln P_i. \quad (2.4.15)$$

Questions regarding the problem of pressure units are resolved in the same manner as for the entropy equations, with minor modifications: On account of (2.4.12b) $\mu_i^{OP}(T)$ now involves the quantity \tilde{E}_0 , and therefore is specified only to within an arbitrary constant, as is appropriate for a quantity that represents a generalized energy. However, the same constant is relevant to both $\mu_i(T, P_i)$ and $\mu_i^{OP}(T)$ and thus is immaterial. One should carefully note that, appearances to the contrary, $\mu_i(T, P_i)$ as specified by Eq. (2.4.15) is independent of the choice of pressure units, since (2.4.15) is merely a special case of (2.4.14) where the logarithmic argument is independent of the units. By contrast the quantities $\mu^{OP}(T)$ and $RT \ln P_i$ do depend on the choice of units, in such a manner that changes cancel out from their algebraic sum.

Equation (2.4.15) serves as a prototype for chemical potentials in other types of situations involving reversible changes and will be referred to as a *canonical form*.

Adiabatic Changes in the State of an Ideal Gas

Here we begin with the relation $dE = CVdT = dW = -PdV$, which holds for a reversible adiabatic expansion of an ideal gas. By definition C_V is a constant. We immediately find that

$$C_V dT = -nRTdV/V, \quad (2.4.16)$$

which may be integrated between the limits T_1, V_1 and T_2, V_2 . On reverting to molar quantities we find that

$$\tilde{C}_V \ln(T_2/T_1) = -R \ln(V_2/V_1) = R \ln(V_1/V_2). \quad (2.4.17)$$

We now substitute $\tilde{C}_P - \tilde{C}_V$ for R and set $\tilde{C}_P/\tilde{C}_V \equiv \gamma$. Then Eq. (2.4.17) assumes the form

$$\ln(T_2/T_1) = (\gamma - 1) \ln(V_2/V_1), \quad (2.4.18a)$$

or alternatively,

$$T_2/T_1 = (V_1/V_2)^{R/\tilde{C}_V}, \quad (2.4.18b)$$

that is to say, the product TV^{R/\tilde{C}_V} for an ideal gas is a constant under adiabatic changes.

By substitution of $V = nRT/P$ or of $T = PV/nR$ there is no difficulty in proving that for an ideal gas under reversible adiabatic conditions the following relations hold:

$$T_2/T_1 = (P_2/P_1)^{R/\tilde{C}_P}, \quad (2.4.19)$$

and

$$P_1/P_2 = (V_2/V_1)^\gamma \quad \text{or} \quad PV^\gamma = \text{const.} \quad \gamma \equiv \tilde{C}_P/\tilde{C}_V \quad (2.4.20)$$

These are standard expressions cited in the literature. The above relation should be contrasted with the constancy of PV under isothermal conditions.

Reprise on the Temperature Scale

We are now in a position to reexamine the relation between the temperature scales based on the Carnot efficiency (Section 1.11) and on the equation of state for an ideal gas. Referring back to Eq. (1.11.3), let the Carnot engine execute one cycle while operating *reversibly* between two immense hot and cold reservoirs. These are maintained at temperatures θ_h and θ_c , as indicated on the engine thermometers when the engine is individually fully equilibrated with each of the reservoirs. An ideal gas container is also allowed to equilibrate with those same reservoirs during certain stages of the Carnot cycle; the gas thermometer in equilibrium with the same reservoirs registers the corresponding temperatures as T_h and T_c .

The requisite heat exchanges Q_h and Q_c to which the engine is subjected during one cycle are governed by Eq. (1.11.3): $Q_h/\theta_h - \overline{Q}_c/\theta_c = 0$. As stated in Section 1.11 this result obtains no matter what is used as the working substance in the engine. We next focus on what happens to the ideal gas in the above process. We subject it to the following steps: (1) The gas in its initial state is expanded isothermally and reversibly while anchored at the hot reservoir, where T_h is registered as the temperature on the gas thermometer. The process is carried through until the gas has absorbed the same amount of heat Q_h as was absorbed by the Carnot engine. (2) The gas container is detached and cooled reversibly by adiabatic expansion until it can be attached without heat transfer to the cold reservoir, where the engine and gas thermometers register temperatures θ_c and T_c , respectively. (3) The gas is then subjected to a reversible isothermal compression while locked onto the cold reservoir until heat \overline{Q}_c , equal to that of the Carnot engine, has been expelled reversibly into the cold reservoir. (4) The gas container is then detached and subjected to a reversible adiabatic compression, whereby its temperature is caused to rise until the gas is returned to its initial state, after which it is ready for another cycle. The net heat transfer in the above steps is $Q_h - \overline{Q}_c$. Since the entropy changes associated with the reversible adiabatic expansion and compression processes cancel each other out, this leaves a net entropy change of the gas during one cycle as $Q_h/T_h - \overline{Q}_c/T_c = 0$. This result should be compared with the format $Q_h/\theta_h - \overline{Q}_c/\theta_c = 0$ cited above for the Carnot engine. It is evident that the temperature scales associated with the Carnot engine and with the ideal gas must be identical since the same thermal reservoirs were used in the two processes. But the Carnot engine makes no reference to any materials properties; thus, no matter the working substance, the temperature scale of the engine must be identical to that of the ideal gas. We have attained a universal, i.e., a truly thermodynamic, T scale.

Exercises

2.4.1. Establish that $(\partial C_p/\partial P)_T = 0$.

2.4.2. Verify Eqs. (2.4.19) and (2.4.20).

2.5 Properties of Ideal Solutions in Condensed Phases

Fundamental Characterization of Condensed Phases in Solution

A problem of obvious importance is the determination of the chemical potential of constituents that form a liquid or solid solution. We proceed by analogy to Eq. (2.4.15) for the ideal gas mixture. This objective is sensible, at least for ideal solutions defined below, because the different constituents in an ideal

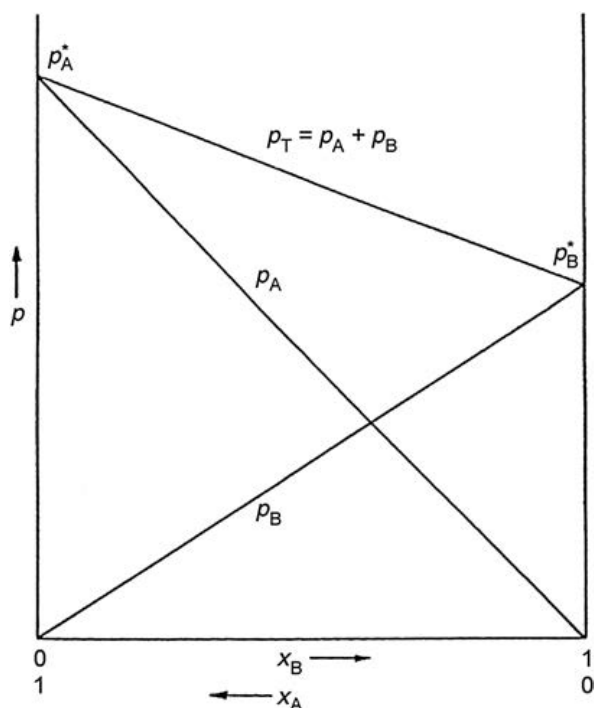


FIGURE 2.5.1

Raoult's law for binary solutions.

condensed phase do not interact, so they form an analog to the ideal gas mixture for which the partial pressure P_i constitutes the independent variable. The corresponding composition variable is the mole fraction x_i . The solutions must be sufficiently dilute for the ideal liquid model, discussed below, to apply.

An *ideal solution* is one for which three criteria must be satisfied:

(1) There shall be no volume change in preparing the solution from its individual components. Then, for all i , \tilde{V}_i^* , the molar volume of pure i , must match \bar{V}_i , its partial molal volume in solution. (2) There shall be no enthalpy change in the mixing process. Let \tilde{H}_i^* and \bar{H}_i represent the molar and partial molal enthalpies of i in the pure state and in the final solution, respectively. Then the equality $\tilde{H}_i^* = \bar{H}_i$ shall apply to every i . (3) *Raoult's law* shall be obeyed: the partial pressure of species i in the gas phase in equilibrium with the solution shall be specified by $P_i = x_i P_i^*$, where x_i is the mole fraction of i in solution, and P_i^* is the equilibrium vapor pressure of the pure component. An illustration of Raoult's edict for a binary phase is furnished by Figure 2.5.1; the asterisks refer to pure phases.

We next show that the above criteria are indeed met, as prescribed, by postulating the following *canonical form* for the chemical potential of species i in an ideal solution:

$$\mu_i(T, P, x_i) = \mu_i^*(T, P) + RT \ln x_i, \quad (2.5.1)$$

where $\mu_i^*(T, P)$ is the chemical potential of pure i , for which $x_i = 1$; this quantity depends parametrically on T and P . The above equation reduces to an identity for $x_i = 1$.

We now verify that Eq. (2.5.1) does indeed satisfy all criteria for an ideal solution: (1) Since $(\partial G / \partial P)_{T, x_i} = V$ and $(\partial G / \partial n_i)_{T, P, n_{j \neq i}} \equiv \mu_i$,

$$\frac{\partial^2 G}{\partial n_i \partial P} = \left(\frac{\partial V}{\partial n_i} \right)_{T,P} = \bar{V}_i = \frac{\partial^2 G}{\partial P \partial n_i} = \left(\frac{\partial \mu_i}{\partial P} \right)_{T,n_i} = \left(\frac{\partial \mu_i^*}{\partial P} \right)_{T,n_i} = \bar{V}_i^*. \quad (2.5.2)$$

It follows that the molar volumes occupied by i in the pure state and in solution are identical. (2) From Eq. (1.12.14b) and (2.5.1) we find that

$$\left[\frac{\partial(\mu_i/T)}{\partial T} \right]_{P,x_j} = \left[\frac{\partial(\mu_i^*/T)}{\partial T} \right]_{P,x_j} = -\frac{\bar{H}_i}{T^2} = -\frac{\tilde{H}_i^*}{T^2}. \quad (2.5.3)$$

Thus, the molar enthalpy of i in solution and in the pure phase are the same, so that the enthalpy of the formation of the solution from its components is zero. (3) From the constraints for equilibrium between liquid and vapor for each species (2.4.15) and (2.5.1) we obtain

$$\mu_i^{OP}(T) + RT \ln P_i = \mu_i^*(R, P) + RT \ln x_i. \quad (2.5.4)$$

Hence, at constant T and P ,

$$\ln P_i = -(1/RT) [\mu_i^{OP}(T) - \mu_i^*(T, P)] + \ln x_i. \quad (2.5.5)$$

The above is equivalent to the relation $P_i = Cx_i$, where C is a parameter that is fixed by requiring that at $x_i = 1$, $P_i = P_i^*$. Equation (2.5.5) thus reads

$$P_i = x_i P_i^*. \quad (2.5.6)$$

In other words, Raoult's law is satisfied.

Thus, the canonical form (2.5.1) does satisfy the criteria for the properties of ideal solutions. One should note that in Eq. (2.5.1) the chemical potential of i is referred to that of pure i , independently of the other component in the solution.

Standard Chemical Potentials

While Eq. (2.5.1) is satisfactory it does relate the chemical potential to reference values that change with pressure. A greater degree of uniformity may be achieved by referring all chemical potentials of solutions to the chemical potentials of the pure constituents under *standard conditions*, $P = 1$ bar, as follows:

$$\mu_i(T, P, x_i) = \mu_i^*(T, 1) + RT \ln x_i. \quad (2.5.7a)$$

Here $\mu_i^*(T, 1)$ is known as the *standard chemical potential for the pure material* at temperature T . This is adopted regardless of the pressure under which the actual experiments are performed. The difficulty is that Eq. (2.5.7a) does not reduce to an identity for pure materials. However, the difference between $\mu_i^*(T, P)$ and $\mu_i^*(T, 1)$ is slight; it may be determined by integration of Eq. (1.12.12) as applied to pure condensed phases undergoing reversible processes: at a fixed temperature T

$$\frac{\mu_i^*(T, P)}{RT} = \frac{\mu_i^*(T, 1)}{RT} + \int_1^P \frac{\tilde{V}_i^*(T, P)}{RT} dp \approx \frac{\mu_i^*(T, 1)}{RT} + \frac{\tilde{V}_i^*(T, P)}{RT} (P - 1). \quad (2.5.7b)$$

This relation relies on the fact that the volume of condensed phases changes only slightly with pressure, and that experiments on solutions are ordinarily carried out under conditions close to 1 bar. Normally,

the last term is negligible compared to its predecessor. It is in this sense that the quantities $\mu_i^*(T, P)$ and $\mu_i^*(T, 1)$ may be used interchangeably. A better treatment of this problem will be offered in Section 3.3.

Thermodynamic Characterization of Ideal Solutions

We first derive several thermodynamic quantities that pertain to the mixing of constituents to form ideal solutions: Let G be the total Gibbs free energy of the solution and let \tilde{G}_i^* be the molar Gibbs free energy of constituent i in pure form. Then the Gibbs free energy of mixing is given by

$$\Delta G \equiv G - \sum_i n_i \mu_i^* = \sum_i n_i [\mu_i^* + RT \ln x_i] - \sum_i n_i \mu_i^* = RT \sum_i n_i \ln x_i. \quad (2.5.8)$$

By putting everything on a molar basis via $\Delta \tilde{G} \equiv \Delta G / \sum_j n_j$, we obtain the more symmetric relation

$$\Delta \tilde{G} = RT \sum_i x_i \ln x_i. \quad (2.5.9)$$

This relationship will later be used to show how the mixing process is affected by temperature changes. The entropy of mixing under reversible conditions is found from the relation $\Delta \tilde{S} = -\Delta \tilde{G}/T$, since $\Delta \tilde{H} = 0$. We obtain

$$\Delta \tilde{S} = -R \sum_i x_i \ln x_i. \quad (2.5.10)$$

Since all x_i are nonnegative and less than unity the entropy of mixing is indeed positive; this rationalizes the experimental fact that the mixing of components to form an ideal solution is always spontaneous: coffee and cream may readily be mixed, while the reverse process is much harder to achieve. Also, in view of conditions (1) and (2), $\Delta \tilde{E} = \Delta \tilde{C}_P = \Delta \tilde{C}_V = 0$.

The chosen unit for concentration is the mole fraction. The use of other variables, such as molarity or molality is also common, but leads to more elaborate relations that will not be discussed here. If you are interested in such details please refer to a source where these matters are extensively covered.¹

Reference

2.5.1. See, e.g., J.M. Honig *Thermodynamics* (Academic Press, Amsterdam, 2007), 3rd Ed., Sections 2.5.3–2.5.5.

2.6 The Duhem–Margules Equation and Its Consequences

We study the consequences of applying the Gibbs–Duhem relation to a two-component system at constant T and P . This should make that relationship appear much less abstract: it imposes important restrictions on components in equilibrium. We proceed as follows: Divide the relation $n_1 d\mu_1 + n_2 d\mu_2 = 0$ by $(n_1 + n_2)$ to obtain $x_1 d\mu_1 + (1 - x_1) d\mu_2 = 0$. With $dx_2 = -dx_1$ we find that

$$\begin{aligned} x_1 (\partial \mu_1 / \partial x_1)_{T,P} dx_1 + x_2 (\partial \mu_2 / \partial x_2)_{T,P} dx_2 &= x_1 (\partial \mu_1 / \partial x_1)_{T,P} dx_1 \\ + (1 - x_1) (\partial \mu_2 / \partial x_1)_{T,P} dx_1 &= 0, \end{aligned} \quad (2.6.1)$$

which may be rewritten as

$$\begin{aligned}
 (\partial\mu_1/\partial\ln x_1)_{T,P} dx_1 - \left[(\partial\mu_2/\partial\ln(1-x_1))_{T,P} dx_1 \right] &= (\partial\mu_1/\partial\ln x_1)_{T,P} dx_1 \\
 -(\partial\mu_2/\partial\ln x_2)_{T,P} dx_1 &= 0.
 \end{aligned}
 \tag{2.6.2}$$

Now set $d\mu_i|_{T,P} = RTd \ln P_i$ for both components to write

$$(\partial \ln P_1 / \partial \ln x_1)_{T,P} = (\partial \ln P_2 / \partial \ln x_2)_{T,P}, \tag{2.6.3}$$

which is the so-called *Duhem–Margules* equation. It now follows that if Raoult's law applies to one component of a binary solution it applies to the second component as well. For, suppose that $P_1 = x_1 P_1^*$, where, at constant T and P , P_1^* is fixed. Then, with $(\partial \ln P_1 / \partial \ln x_1)_{T,P} = 1$ we find that $(\partial \ln P_2 / \partial \ln x_2)_{T,P} = 1$, as follows from Eq. (2.6.3). Integration then yields $P_2 = x_2 P_2^*$, as was to be proved.

The composition of the vapor phase, relative to that of the liquid phase in equilibrium with it, is found from

$$P = x_1 P_1^* + x_2 P_2^* = x_1 P_1^* + (1 - x_1) P_2^* = P_2^* + x_1 (P_1^* - P_2^*) = P_1^* + x_2 (P_2^* - P_1^*). \tag{2.6.4}$$

which indicates a linear dependence of the total pressure on the mole fraction of either component, as is illustrated in Figure 2.6.1.

The composition of the gas phase may be ascertained as follows: Let the mole fractions in the gas phase be indicated by primes; then

$$x_1' / x_2' = P_1 / P_2 = x_1 P_1^* / x_2 P_2^* = x_1' / (1 - x_1') = x_1 P_1^* / (1 - x_1) P_2^*. \tag{2.6.5}$$

On eliminating x_1 between Eqs. (2.6.4) and (2.6.5) we find that

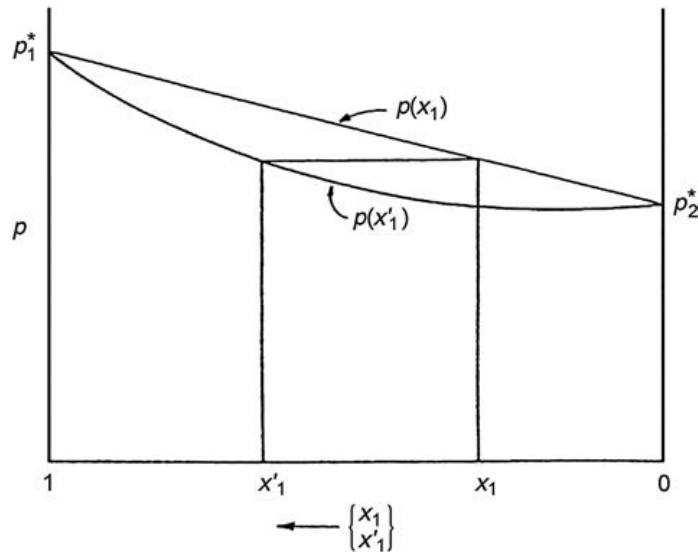


FIGURE 2.6.1

Equilibrium vapor pressure of a liquid solution as a function of the mole fraction of component 1 in the liquid phase (x_1) and in the vapor phase (x_1').

$$P = \frac{P_1^* P_2^*}{P_1^* - x_1' (P_1^* - P_2^*)}. \quad (2.6.6)$$

One notes that P is linear in x_1 , whereas this is not the case in the above relation. The vapor phase is richer in the more volatile component: for, if $P_1^* > P_2^*$, then, by Eq. (2.6.5), $x_1'/(1 - x_1') > x_1/(1 - x_1)$, or $x_1' > x_1$. These findings are illustrated in Figure 2.6.1.

2.7 Temperature Dependence of Composition of Solutions

We need to examine the effects of changes in temperature on the composition of a binary solution in equilibrium with the vapor phase. The situation is somewhat complicated because the composition of the two phases, as well as the total pressure, is altered with temperature changes. For, an increase in T favors the evaporation of the more volatile component, thereby enriching the gas phase and depleting the liquid phase of this component. Thus, both x_i and x_i' are changed, even though the overall composition of the closed system remains the same. To simplify matters we impose the additional restriction that the total pressure remain fixed. This may be done in principle by use of a moveable piston. We now invoke the equilibrium constraint for each species: $\mu_i(g) = \mu_i(l)$. Then, according to Eqs. (2.4.15) and (2.5.1),

$$\mu_i^{OP}(T) + RT \ln P_i = \mu_i^*(T, 1) + RT \ln x_i. \quad (2.7.1)$$

Differentiating both sides with respect to T yields

$$\left[\frac{\partial}{\partial T} \left(\frac{\mu_i^{OP}}{RT} \right) \right]_P + \left(\frac{\partial \ln P_i}{\partial T} \right)_P = \left[\frac{\partial}{\partial T} \left(\frac{\mu_i^*}{RT} \right) \right]_P + \left(\frac{\partial \ln x_i}{\partial T} \right)_P. \quad (2.7.2)$$

The partial pressure of i is specified by $P_i = x_i' P$, in which the presence of any inert gas must be taken into account in specifying x_i' . Insertion into the above leads to

$$\left[\frac{\partial}{\partial T} \left(\ln \frac{x_i'}{x_i} \right) \right] = \left[\frac{\partial}{\partial T} \left(\frac{\mu_i^* - \mu_i^{OP}}{RT} \right) \right]_P = - \frac{\tilde{H}_i^* - \tilde{H}_i^0}{RT^2} = - \frac{\bar{H}_i^* - \bar{H}_i'}{RT^2}, \quad (2.7.3)$$

where we first utilized Eq. (2.5.3) and then introduced criterion (2) for the constituents of an ideal mixture: \tilde{H}_i^* and \tilde{H}_i^0 for the isolated components are equal, respectively, to the partial molal enthalpies of the same constituents in solution (\bar{H}_i) and in the vapor phase (\bar{H}_i'). As shown above, the relative changes in composition are linked to changes in the enthalpy, which accords with the description, furnished earlier, on the effects of changing the temperature.

The above derivation is not restricted to just miscible solutions. With appropriate changes in interpretation it holds equally well for any other two-phase mixture, including liquid solutions in equilibrium with solid solutions, or, more importantly, to a liquid solution in equilibrium with a pure solid component (such as ice immersed in a salt solution). In that case $x_i' = 1$ refers to the pure component and we obtain

$$(\partial \ln x_i / \partial T)_P = \Delta H_f / RT^2, \quad (2.7.4)$$

where ΔH_f is the enthalpy of fusion of the pure solid. This matter will be taken up in much greater detail in the next section.

2.8 Lowering of the Freezing Point and Elevation of the Boiling Point of a Solution

An interesting problem in solution thermodynamics concerns the change in freezing and boiling points of a solvent containing different quantities of solute. As is experimentally well established, the addition of a material B that dissolves in liquid A causes a lowering of the freezing point of the solution relative to the freezing point of the pure solvent. As an example, let A and B represent water and sugar, respectively; at the freezing point the sugar solution is in equilibrium with pure ice. More generally, we look for an analytic relation that shows how much the freezing point of a pure solvent is depressed when a given quantity of solute is dissolved in the solvent, without precipitating the additive.

Depression of the Freezing Point

For pure solid A (e.g., ice) to be in equilibrium with the solution containing B dissolved in liquid A (e.g., sugar in water) requires the chemical potential μ_A to be the same in both phases:

$$\mu_A^*(T, P) = \mu_1^*(T, P) + RT \ln x_1, \quad (2.8.1)$$

where μ_A^* and μ_1^* are the chemical potentials of pure A in the solid (e.g., ice) and in the liquid state (e.g., water), respectively. This is the fundamental relation on which the subsequent derivation is based.

Note the implication of the equilibrium condition (2.8.1), which links x_1 (e.g., the mole fraction of water) to T and to P . Thus, at constant P , a given temperature corresponds to a particular composition, x_1 , of the solvent, and vice versa; we write $x_1 = x_1(T)$. To investigate this dependence it is *à propos* to carry out a partial differentiation of Eq. (2.8.1) with respect to T :

$$-\left\{ \partial [(\mu_1^* - \mu_A^*)/RT] / \partial T \right\}_P = (\tilde{H}_1^* - \tilde{H}_A) / RT^2 \equiv \tilde{L}_f / RT^2 = (\partial \ln x_1 / \partial T)_P. \quad (2.8.2)$$

In this expression we have first invoked Eq. (1.12.14b) or, alternatively, Eq. (2.7.3) in different notation: \tilde{H}_1^* and \tilde{H}_A^* are the molar enthalpies of pure liquid A and of pure solid A, respectively. \tilde{L}_f represents the molar heat of fusion of pure A, not the molar enthalpy change for the transfer of pure A into the solution A + B. Lastly, we invoked Eq. (2.8.1) to obtain the quantity on the right.

Equation (2.8.2) may be integrated as shown:

$$-\int_1^{x_1} d \ln x_1 = -\int_{T_f}^{T_1} (\tilde{L}_f / RT^2) dT, \quad (P \text{ constant}) \quad (2.8.3)$$

where the limits on the integrals correspond to two different conditions: T_f is the freezing point of pure A ($x_1 = 1$), and T_1 is the freezing point of the solution for which the mole fraction of A is x_1 . In Exercise 2.8.1, the reader is asked why, on physical grounds, a change in T brings about a change in composition of the solution.

We must take account of the temperature dependence of \tilde{L}_f , in first order, via the *Kirchhoff relation*, $(\partial \tilde{L}_f / \partial T)_P = (\tilde{C}_P^*)_1 - (\tilde{C}_P^*)_A \equiv \Delta \tilde{C}_P$, where $\Delta \tilde{C}_P$ represents the difference in molar heat capacity of pure liquid A and pure solid A. If the temperature dependence of this difference is negligible we obtain in first approximation the linear dependence

$$\tilde{L}_f = \tilde{L}_f^0 + \Delta\tilde{C}_P(T - T_f), \quad (2.8.4)$$

where \tilde{L}_f^0 is the value of \tilde{L}_f at the freezing point, T_f . Then at fixed P

$$-\int_1^{x_1} d \ln x_1 = -\int_{T_1}^{T_f} \left[\tilde{L}_f^0 / RT^2 + (\Delta\tilde{C}_P / RT^2) (T - T_f) \right] dT. \quad (2.8.5)$$

Next, define the lowering of the freezing point by

$$\Theta_f \equiv T_f - T_1, \quad (2.8.6a)$$

which allows us to write

$$T_1 = T_f [1 - (\Theta_f / T_f)]. \quad (2.8.6b)$$

Equation (2.8.5) may then be integrated to yield (constant P)

$$\begin{aligned} -\ln x_1 &= \left[\left(\frac{\tilde{L}_f^0}{RT_f} \right) - \left(\frac{\Delta\tilde{C}_P}{R} \right) \right] \left(\frac{T_f - T_1}{T_1} \right) - \left(\frac{\Delta\tilde{C}_P}{R} \right) \ln \left(\frac{T_1}{T_f} \right) \\ &= \left[\frac{\tilde{L}_f^0}{RT_f} - \left(\frac{\Delta\tilde{C}_P}{R} \right) \right] \left[\frac{\Theta_f / T_f}{(1 - \Theta_f / T_f)} \right] - \frac{\Delta\tilde{C}_P}{R} \ln \left[1 - \frac{\Theta_f}{T_f} \right]. \end{aligned} \quad (2.8.7)$$

In general it is an excellent approximation to expand in small powers of Θ_f / T_f . Set $(1 - \Theta_f / T_f)^{-1} \approx 1 + \Theta_f / T_f$ and $\ln(1 - \Theta_f / T_f) \approx -[\Theta_f / T_f + (\Theta_f / T_f)^2 / 2]$. Further, $-\ln x_1 = -\ln(1 - x_2) \approx x_2$. Here x_2 is the mole fraction of the solute. Equation (2.8.7) then reduces to

$$x_2 \approx \left(\tilde{L}_f^0 / RT_f \right) (\Theta_f / T_f) + \left[\left(\tilde{L}_f^0 / RT_f \right) - (\Delta\tilde{C}_P / 2R) \right] (\Theta_f / T_f)^2. \quad (2.8.8)$$

The replacement of $-\ln x_1$ by x_2 does limit the applicability of Eq. (2.8.8) to dilute solutions, but this limitation is clearly essential if the theory of ideal solutions is to serve as a good approximation.

Equation (2.8.8) is a quadratic equation in Θ_f , which may be solved to find Θ_f in its dependence on x_2 . However, with all of the above approximations, we are generally justified in neglecting the quadratic term in $(\Theta_f / T_f)^2$. Equation (2.8.8) may then be inverted to read

$$\Theta_f = \left(RT_f^2 / \tilde{L}_f^0 \right) x_2. \quad (2.8.9)$$

In general usage the lowering of the freezing point is expressed in terms of the molality m_2 of the solute. We now set

$$\frac{m_i}{x_i} = \frac{1000 n_i}{n_1 M_1} \frac{\sum_j n_j}{n_i} = \frac{1000}{x_1 M_1}. \quad (2.8.10a)$$

Then, for very dilute solutions, with $x_1 = 1$, we find that $x_2 / m_2 = M_1 / 1000$, so that

$$\Theta_f \approx \left(RT_f^2 M_1 / 1000 \tilde{L}_f^0 \right) m_2 \equiv K_f m_2. \quad (2.8.10b)$$

This relation is remarkable in several respects. First, in the present approximation the lowering of the freezing point is a linear function of x_2 or m_2 . Second, the proportionality factor K_f depends solely on the properties of the pure solvent (i.e., on M_1 , T_f , and \tilde{L}_f^0) and not on the properties of the solute. For a

fixed solvent K_f is thus predetermined and is maximized for solvents with high freezing points, high molecular weights, and low heats of fusion. All these accord with most experiments; in fact, in the early days of chemical research, the determination of the freezing point depression was used to find the molecular weight of many materials. However, numerical estimates based on Eq. (2.8.10) fail in cases where solutes associate or dissociate. The analysis of this situation is left as an exercise. Also, allowance must be made for cases where the solvent ionizes when going into solution. This problem is addressed in Chapter 4.

Elevation of the Boiling Point

The foregoing procedure requires small changes to become applicable to the elevation of the boiling point T_b for an ideal solution containing nonvolatile solutes and a volatile solvent. The equilibrium constraint for the solvent now reads

$$\mu_1^*(T, P) + RT \ln x_1(l) = \mu_1^{OX}(T, P) + RT \ln x_1(g), \quad (2.8.11)$$

where l and g refer to the liquid and gaseous phases. Accordingly [note Eq. (2.7.3)],

$$-\left[\frac{\partial}{\partial T} \left(\frac{\mu_1^{OX} - \mu_1^*}{RT} \right)\right]_P = \frac{\tilde{H}_1^0 - \tilde{H}_1^*}{RT^2} = \left[\frac{\partial \ln x_1[(g)/x_1(l)]}{\partial T} \right]_P. \quad (2.8.12)$$

Consider the case where the solvent vapor alone constitutes the gas phase (e.g., a sugar solution in equilibrium with steam). In that event $x_1(g) = 1$, and we can then set $x_1(l) \equiv x_1$. Equation (2.8.12) now reduces to

$$(\partial \ln x_1 / \partial T)_P = -(\tilde{H}_1^0 - \tilde{H}_1^*) / RT^2 = -\tilde{L}_v / RT^2, \quad (2.8.13)$$

where \tilde{L}_v is the molar heat of vaporization of component A from the pure liquid to the gas phase. If P is set at 1 bar one deals with the normal boiling point. We now

1. rewrite Eq. (2.8.13) as

$$-d \ln x_1|_P = (\tilde{L}_v / RT^2) dT|_P, \quad (2.8.14)$$

2. introduce Kirchhoff's law in the approximation

$$\tilde{L}_v = \tilde{L}_v^0 + (\tilde{C}_P^g - \tilde{C}_P^l)(T - T_b), \quad (2.8.15)$$

3. introduce the elevation of the boiling point by the definition $\Theta_b \equiv T_1 - T_b$, so that $T_1 = T_b(1 + \Theta_b/T_b)$, and

4. expand $(1 + \Theta_b/T_b)^{-1}$, as well as $\ln(1 + \Theta_b/T_b)$ in powers of Θ_b/T_b . This yields

$$-\ln x_1 \approx x_2 = \left(\tilde{L}_v^0 / RT_b \right) (\Theta_b / T_b) - \left[\left(\tilde{L}_v^0 / RT_b \right) - (\Delta \tilde{C}_P / 2R) \right] (\Theta_b / T_b)^2. \quad (2.8.16)$$

On neglect of the last term on the right, the resulting equation may be inverted to read

$$\Theta_b = \left(RT_b^2 / \tilde{L}_v^0 \right) x_2 \quad (2.8.17)$$

and

$$\Theta_b = \left(RT_b^2 M_1 / 1000 \tilde{L}_v^0 \right) m_2 \equiv K_b m_2. \quad (2.8.18)$$

The various remarks made in conjunction with Eq. (2.8.10) also apply here with appropriate modifications.

Exercise

2.8.1. Provide a physical explanation why the freezing point of a solvent is lowered when solute is added to form a solution.

2.9 General Description of Chemical Reactions and Chemical Equilibrium; Application to Gases

Representation of Chemical Equations

Now, onto one of the most important applications of thermodynamics to chemistry, namely, the treatment of chemical reactions and chemical equilibrium. We first develop some general principles. Consider the prototype of a chemical reaction, $\nu_{1r}R_1 + \nu_{2r}R_2 + \dots = \nu_{1p}P_1 + \nu_{2p}P_2 + \dots$, in which, for the reaction *as written*, R_1, R_2, \dots are different chemical reagents, P_1, P_2, \dots are different chemical products, and the ν_{ir}, ν_{ip} are stoichiometry coefficients for reagents and products, respectively. The writing out of a balanced chemical reaction is not unique; it might have been written with reagents and products reversed, or with different numerically proportional values for the stoichiometric coefficients. However, once adopted, the chemical reaction must be kept unaltered in the subsequent analysis.

It is convenient to abbreviate the above schematic reaction as

$$\sum_i \nu_i A_i = 0. \quad (2.9.1a)$$

in which, by convention, the ν_i are negative or positive according as the chemical species A_i designate reagents or products, *for the reaction as written*.

In what follows we must distinguish two cases: The first relates to a chemical reaction in progress which has been interrupted at some stage by imposition of some constraints (such as sudden cooling, or coupling to an electrolytic cell, as described in Section 4.7). In our standard notation the Gibbs free energy is given by $G = \sum_i n_i \mu_i$, where the mole numbers and chemical potentials of the various species now refer to their values in the arrested stage at a specified T and P . The second involves letting the reaction proceed at fixed T and P until it has run its course, halts, and remains at equilibrium, where the $n_i|_{eq}$ and $\mu_i|_{eq}$ are the then prevailing mole numbers and chemical potentials.

Consider first the quiescent situation. As before, it is characterized by studying a virtual displacement of the above reaction (see Section 1.9) from its constrained configuration at a fixed pressure and temperature. This process must be carried out reversibly; for example, one may change the composition by slow insertion and removal of chemical species, or by slightly altering the

potentiometer setting of an electrolytic cell, as explained in Sections 4.4 and 4.5. The corresponding Gibbs free energy change is given by

$$\delta G = \sum_i \mu_i \delta n_i + \sum_i n_i \delta \mu_i = \sum_i \mu_i \delta n_i, \quad (\text{constant } T, P) \quad (2.9.1b)$$

To justify the last step, refer back to Section 1.14, where it was shown that slight departures from the arrested process cannot be executed arbitrarily but are subject to constraints imposed by the Gibbs–Duhem relation, according to which the sum $\sum_i \mu_i \delta n_i$ vanishes at constant T and P .

Virtual displacements involving chemical reactions are also subject to another constraint, namely, that the individual mole numbers n_i must change in proper synchronization, so as to accord with the stoichiometry requirements of the chemical reaction. This can be guaranteed by introducing an infinitesimal, virtual (which also implies “reversible”) unit of advancement, $\delta\lambda$, of the entire chemical reaction $\sum_i \nu_i A_i = 0$, such that the changes in the various mole numbers are expressed by $\delta n_i = \nu_i \delta\lambda$. Then Eq. (2.9.1b) reads

$$\delta G = \sum_i \mu_i \delta n_i = \left(\sum_i \nu_i \mu_i \right) \delta\lambda \equiv (\Delta G_d) \delta\lambda, \quad (T, P \text{ constant}). \quad (2.9.2a)$$

Here we have introduced the definition

$$\Delta G_d = (\delta G / \delta\lambda)_{T,P} = \sum_i \nu_i \mu_i|_{T,P}. \quad (2.9.2b)$$

One must be very careful concerning the interpretation of the quantity ΔG_d ; as indicated by the defining relation, it is a *differential Gibbs free energy change per unit advancement of the reaction*.¹ This accompanies an infinitesimal reversible change in mole numbers at any constrained stage of the reaction process at constant T and P , which essentially preserves the number of moles n_i of every species i participating in the reaction.² The quantity ΔG_d may be calculated, as shown in Eq. (2.9.2b), from the chemical potentials μ_i prevailing in the mixture during the infinitesimal, reversible advancement of the reaction, while keeping the constraints in place. This calculation differs from the determination of the integral Gibbs free energy change that characterizes the changes in mole numbers when a chemical reaction is carried to completion. Note that if $\sum_i \nu_i A_i < 0$ (>0) the reaction as written occurs spontaneously (in the opposite direction).

We now take up the case where chemical equilibrium prevails. In this event the constraint $(\delta G / \delta\lambda)_T = 0$ must be taken into account; it guarantees that G has reached a minimum under the applicable constraints. This leads to the important condition characterizing chemical equilibrium, namely,

$$\sum_i \nu_i \mu_i|_{eq} = 0. \quad (2.9.3)$$

We must now investigate the ramifications of this important requirement.

Chemical Equilibrium in Gas Phases

For an ideal homogeneous gaseous system, $\mu_i = \mu_i^{OP}(T) + RT \ln P_i$ [see Eq. (2.4.15)], so that the equilibrium condition Eq. (2.9.3) reads

$$0 = \sum_i \nu_i \mu_i^{OP}(T) + RT \left(\sum_i \nu_i \ln P_i \right)_{eq}. \quad (2.9.4)$$

It is useful to rewrite Eq. (2.9.4) as follows:

$$-\sum_i \nu_i \mu_i^{OP}(T)/RT \equiv \ln K_P(T) = \left(\sum_i \nu_i \ln P_i \right)_{eq}. \quad (2.9.5a)$$

Here we have separated out various terms such that the left-hand side is a parametric function of T alone, while the right-hand side depends on the characteristics and composition of the gas mixture. It is therefore appropriate to introduce, as in Eq. (2.9.5a), a new quantity K_P , which shows explicitly that the left-hand side is actually independent of composition variables. K_P is termed an *equilibrium constant*—a highly undesirable appellation because this quantity obviously varies with T and thus ought to be designated an “equilibrium parameter”. However, the term “equilibrium constant” is so firmly entrenched that we shall continue to use it here. A convenient reformulation of Eq. (2.9.5a) is found by taking antilogarithms:

$$K_P(T) = \prod_i (P_i^{\nu_i})_{eq}. \quad (2.9.5b)$$

The equilibrium constant actually involves a ratio of partial pressures, since the stoichiometry coefficients ν_i of the reagents are negative. Equation (2.9.5b) is in the standard form used to specify equilibrium constants in terms of prevailing equilibrium composition variables, in this case, the partial pressures. Thus, the expression on the left-hand side requires that the exponentiated partial pressure ratios on the right-hand side are subject to a new constraint; they are interrelated by a function of T .

Free Energy Changes of Reactions in the Gas Phase

The evaluation of ΔG_d is of considerable interest. In the general case, when equilibrium does not prevail, the mole numbers n_i are arbitrary. If at any fixed stage the reaction $\sum_i \nu_i A_i = 0$ is arrested and then advanced infinitesimally and reversibly at constant T and P , we may set

$$\Delta G_d = \sum_i \nu_i \mu_i^{OP}(T) + RT \sum_i \nu_i \ln P_i \quad (2.9.6a)$$

$$= -RT \left(\sum_i \nu_i \ln P_i \right)_{eq} + RT \sum_i \nu_i \ln P_i \quad (2.9.6b)$$

$$= -RT \ln K_P + RT \sum_i \nu_i \ln P_i, \quad (2.9.6c)$$

where we have inserted Eqs. (2.9.2b), (2.9.5a) and (2.4.15) on the right-hand side. Here and below it is of the utmost importance to distinguish between $\sum_i \nu_i \ln P_i$, which merely has the same form as $\ln K_P$, from $(\sum_i \nu_i \ln P_i)_{eq}$, which is identical with $\ln K_P$. The partial pressures P_i are those appropriate to the instantaneous conditions at any arrested stage of the chemical reaction. Confusion at this point can be disastrous. As is evident from the discussion of Eq. (2.4.15)—the analog of Eq. (2.9.6a)— K_P depends on the units chosen for gas pressures, i.e., whether in terms of atmospheres, bars, dynes/cm², or whatever. However, the corresponding $\Delta G_d/RT$ is independent of such choices, as is also clear from an examination of Eq. (2.9.6b).

At this stage we introduce the *standard free energy change* ΔG_d^0 for the reaction. This is the value of ΔG_d when the reaction is hypothetically advanced infinitesimally and reversibly while all gaseous constituents are at unit pressure (usually 1 bar) at the temperature of interest. This leads to some

conceptual problems: what if you cannot actually carry out the reaction under such conditions? Actually, one need not be able actually to carry out the reaction step under the above conditions. For, we specify the free energy change as $\Delta G_d^0 = \sum_i \nu_i \mu_i^{OP}(T)$; hence, one can either measure the individual chemical potentials at temperature T and under a pressure of 1 bar (methods for doing so are discussed in Chapters 1 and 4) or look up tabulated values. Equation (2.9.6a) thus reduces to

$$\Delta G_d^0 = -RT \ln K_P \quad \text{or} \quad K_P = \exp(-\Delta G_d^0/RT). \quad (2.9.7)$$

More generally, Eq. (2.9.6c) reads

$$\Delta G_d = \Delta G_d^0 + RT \sum_i \nu_i \ln P_i. \quad (2.9.8)$$

Note that the equilibrium constant K_P is directly related by Eq. (2.9.7) to the differential free energy change of a chemical reaction under standard conditions. Also, the ΔG_d value for the reaction under arbitrary, reversible, isothermal, and isobaric conditions involves the sum of ΔG_d^0 and of a “correction term” $RT \sum_i \nu_i \ln P_i$.

If equilibrium prevails, $\Delta G_d = 0$; in this event Eq. (2.9.8) reduces to

$$\Delta G_d^0 = -RT \left(\sum_i \nu_i \ln P_i \right)_{eq}, \quad (2.9.9a)$$

which is consistent with both Eqs. (2.9.5) and (2.9.7).

The remarks made earlier concerning ΔG_d apply to the quantity ΔG_d^0 in Eqs. (2.9.7–2.9.9), with the additional requirement that all species must be maintained at their standard states during the infinitesimal advancement of the reaction. As already discussed, the definition

$$\Delta G_d^0(T) \equiv \sum_i \nu_i \mu_i^{OP}(T) \quad (2.9.9b)$$

leaves no ambiguity: the chemical potentials are then to be combined³ as required by Eq. (2.9.9b).

Temperature Variation of the Equilibrium Parameter

We now consider the variation of the equilibrium “constant” with temperature. We base our further discussion on Eq. (1.12.14b) and we consider the definitions (2.9.5)–(2.9.7).

$$\frac{d \ln K_P}{dT} = - \sum_i \frac{\nu_i}{R} \frac{d}{dT} \left(\frac{-\mu_i^{OP}}{T} \right) = \frac{\sum_i \nu_i \bar{H}_i^0}{RT^2} \equiv \frac{\Delta H_d^0}{RT^2}. \quad (2.9.10)$$

Equation (2.9.10) is one formulation of *van't Hoff's equation* (1886). The cautionary discussion concerning ΔG_d and ΔG_d^0 also applies to ΔH_d^0 : This represents the differential enthalpy evolution accompanying unit advancement of the reaction $\sum_i \nu_i A_i = 0$ when the latter is changed hypothetically, reversibly, and infinitesimally while maintaining all species in their standard states. No ambiguity results when one uses the definition $\Delta H_d^0 = \sum_i \nu_i \bar{H}_i^0$. Since \bar{H}_i^0 arose through the partial differentiation in Eq. (2.9.10) it represents the partial molal enthalpy of species i at temperature T under standard conditions. This quantity is usually available in tabulations.

In practice Eq. (2.9.10) and its analogs are frequently used in reverse. For ideal gas mixtures $d(\mu_i^0/T)/dT$ and $d(\mu_i/T)/dT$ are identical; hence, $\Delta H_d^0 = \Delta H_d = \sum_i \nu_i \bar{H}_i$, so that we may write

$$\Delta H_d = RT^2(d \ln K_P/dT), \quad (2.9.11)$$

which shows that if the variation of K_P with T is known empirically or from a theoretical analysis, ΔH_d may be found for the gaseous reaction $\sum_i \nu_i A_i = 0$. Note further that by integration of Eq. (2.9.11),

$$\ln[K_P(T_2)/K_P(T_1)] = \int_{T_1}^{T_2} (\Delta H_d/RT^2) dT, \quad (2.9.12)$$

which requires that one specify the dependence of ΔH_d on T . Here Kirchhoff's law may be used if no other detailed information is available.

Statistical Treatment of Chemical Equilibria Involving Gaseous Reactions

The determination of equilibrium constants is obviously of great importance. One route to meet this objective is through the use of statistical thermodynamics. For this purpose we begin with the fundamental relation, Eq. (2.9.7). The specification of the Gibbs free energies for the various gaseous chemical species involves a set of distinct zero point energies for the various degrees of freedom of the different species. By convention, we set the zero point of energy of a compound as the energy at $T = 0$ K of the constituent atoms at infinite separation from each other. This requires the specification of the dissociation energies for the breakage of all the bonds of the *gaseous species* in their hypothetical standard states at 0 K. As is evident from Figure 2.9.1 the ground state for the bond is at energy $\varepsilon_0^o < 0$ relative to the infinite separation distance that corresponds to the zero of energy. The actual energy required for the breaking of the bond is set at $D_0^o > 0$; it is less by $h\nu_{ij}/2$ than $D_{qij}^o > 0$, the energy from the minimum of the potential energy curve to the zero of energy. We therefore set

$$\varepsilon_0^o = -[D_{qij}^o - h\nu_{ij}/2]. \quad (2.9.13)$$

Here i identifies the chemical species, and j enumerates the particular normal mode for that species.

The chemical reaction thus involves dissociation energies of the form

$$\Delta \varepsilon_0^o = -\sum_i \nu_i \sum_{j=1}^{\alpha_i} [D_{qij}^o - h\nu_{ij}/2]. \quad (2.9.14)$$

This energy difference may now be represented by a corresponding molecular partition function of the form

$$q_{D_i} = e^{-\varepsilon_0^o/k_B T} = e^{\sum_{j=1}^{\alpha_i} [D_{qij}^o - h\nu_{ij}/2]}. \quad (2.9.15)$$

The total statistical partition function for species i is given by

$$Q_{D_i} = (q_t q_r q_v q_e q_D)_i^{N_i} / N_i! \equiv (q_{D_i})^{N_i} / N_i!, \quad (2.9.16)$$

while the Helmholtz free energy reads

$$A_i = -k_B T \ln Q_{D_i} \equiv -N_i k_B T \ln q_{D_i} - k_B T \ln Q_i = N_i \varepsilon_0^o - k_B T \ln Q_i, \quad (2.9.17)$$

where Q_i is the ordinary system partition function introduced in Chapter 10. Then

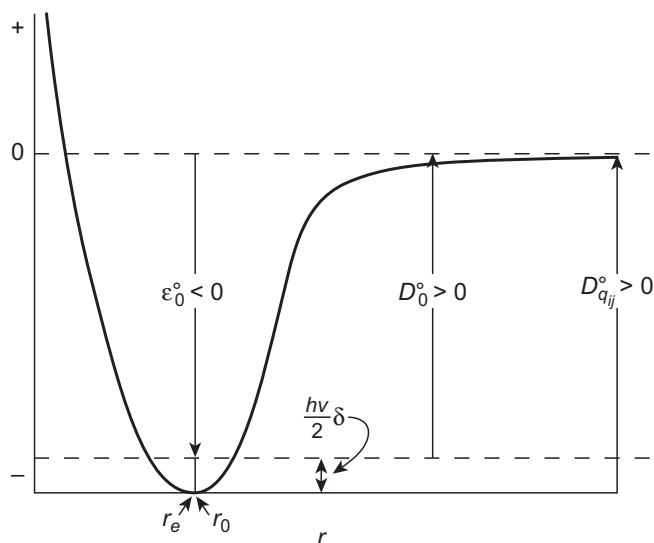


FIGURE 2.9.1

Potential energy diagram vs separation distance between two atoms. Note the various energies relative to the zero of energy at infinite separation. Reproduced from P.A. Rock, *Chemical Thermodynamics*, Copyright University Science Books, Mill Valley, CA; used with permission.

$$A_i = N_i \epsilon_{i0}^o - N_i k_B T - N_i k_B T \ln(q_i/N_i). \quad (2.9.18)$$

For 1 mol of an ideal gas in the standard state the above becomes

$$\tilde{A}_i^0 = N_A \epsilon_{i0}^o - RT - RT \ln(\tilde{q}_i^0/N_A), \quad (2.9.19)$$

so that, on switching to the Gibbs free energy we find that

$$\tilde{G}_i^0 = N_A \epsilon_{i0}^o - RT \ln(\tilde{q}_i^0/N_A), \quad (2.9.20)$$

and for the chemical reaction under standard conditions, denoted by the superscript zero, we obtain

$$\Delta G_d^0 = N_A \sum_i \nu_i \epsilon_{i0}^o - RT \ln \prod_i (\tilde{q}_i^0/N_A)^{\nu_i} = -RT \ln \prod_i (\tilde{q}_i^0/N_A)^{\nu_i} e^{-\Delta \epsilon_0^o/k_B T}, \quad (2.9.21)$$

from which we obtain the statistical mechanical expression for the equilibrium constant in the form

$$K(T) = \exp\left(-\frac{\Delta \epsilon_0^o}{k_B T}\right) \times \prod_i \left(\frac{\tilde{q}_i^0}{N_A}\right)^{\nu_i}. \quad (2.9.22)$$

We may substitute the volume V for N_A in the specification of the translation partition function; since $\tilde{q}_i^0/N_A \equiv (V/N_A)(\tilde{q}_i^0/V) = (k_B T/P)(\tilde{q}_i^0/V)$. With $P = 1$ under standard conditions, Eq. (2.9.22) is transformed to ($\Delta \nu \equiv \sum_i \nu_i$)

$$K(T) = (k_B T)^{\Delta \nu} \exp\left(-\frac{\Delta \epsilon_0^o}{k_B T}\right) \times \prod_i \left(\frac{\tilde{q}_i^0}{V}\right)^{\nu_i}. \quad (2.9.23)$$

This solves the problem—at least in principle. You still need to specify the actual partition function for every one of the equilibrated species. You should also carefully note some caveats: (1) The numerical choice for k_B in the factor $(k_B T)^{\Delta \nu}$ must conform to the conventional choice of units for R . (2) The numerical choice for k_B in the $e^{-\Delta \varepsilon_0^o/k_B T}$ factor must conform to the conventional choice of units for ε_{i0}^o . (3) For obvious reasons, the vibrational partition functions involve factors $(1 - e^{-\Theta_v/T})^{-1}$ not the full expression shown in Eq. (1.12.46). (4) Because of the definitions adopted above, the electronic partition functions, Eq. (1.12.48), involve exponential terms with positive electronic energies $\varepsilon_l > 0$, starting with the ground state at $\varepsilon_l = 0$.

Remarks

- 2.9.1.** The restrictions should be carefully noted. We assume that the reaction has either run its course (at equilibrium) or has been arrested, so that the existing reagents and products are in balance. We then investigate what would happen if this state were slightly perturbed by adding or taking away a tiny set of participating species, keeping all restrictions in place. This operation is to be contrasted with the case in which a chemical reaction proceeds to the extent whereby all starting materials are entirely converted into products. The thermodynamic characterization of such a process differs sharply from the analysis offered here.
- 2.9.2.** For example, the reaction $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ may be carried out reversibly by operating a fuel cell containing n_{H_2} moles of H_2 gas and n_{O_2} moles of O_2 gas in appropriate compartments over the electrodes, and containing $n_{\text{H}_2\text{O}}$ moles of water as the medium into which the electrodes are dipped (see Section 4.5). As long as the cell is operated reversibly by maintaining an appropriate counter electromotive force (emf), so that at the conclusion $n_{\text{H}_2} - 2\delta\lambda$ moles of H_2 gas and $n_{\text{O}_2} - \delta\lambda$ moles of O_2 gas remain in the compartments, and $n_{\text{H}_2\text{O}} + 2\delta\lambda$ moles of water are present, a measurement of the emf yields $\Delta G_d(T, P)$ directly (See Chapter 4 for details; these are not essential to the present argument). However, if the reaction is allowed to proceed to the extent that $\nu_i \delta\lambda$ becomes comparable to the above n_i 's, the mole numbers are no longer constant; the resulting Gibbs free energy change is then no longer identical with the quantity ΔG_d in Eq. (2.9.2). An extreme example is the detonation of 2 mol of H_2 and 1 mol of O_2 in a bomb calorimeter: here the mole numbers are altered to the maximum possible degree, T and P are no longer maintained constant, and the reaction obviously is not carried through reversibly. Any measurement of the total free energy change ΔG for such a process will not even be remotely related to ΔG_d as defined earlier. These examples should alert you to problems that may arise when different authors refer to a free energy change in a reaction; we shall consistently use the subscript d as a reminder of the differential nature of the quantity. Equation (2.9.2) shows clearly that ΔG_d involves the chemical potential μ_i for every species participating in the reaction *under the prevailing steady state or equilibrium conditions*, which remain essentially unaltered in the virtual displacements. Alternatively, one may view ΔG_d as the change in Gibbs free energy when the reaction is carried out such that $\delta\lambda$ equals 1 mol in an essentially infinite copy of the system under study. Obviously, any method by which μ_i can be determined is satisfactory for use in Eq. (2.9.2b); one need not restrict oneself to measurements carried out during an actual reaction.
- 2.9.3.** One may raise the problem of the reference state that should be used in specifying chemical potentials and enthalpies of individual species. This presents no problem here because we

deal with linear summations over all species participating in the reaction; hence, the arbitrarily chosen reference energy, common to all species, cancels out.

2.10 Chemical Equilibrium in Homogeneous Condensed Ideal Solutions

The methods of the previous section will now be extended to deal with equilibrium in homogeneous liquid or solid solutions that form ideal phases. To avoid endless repetitions we assume that all the constraints and caveats mentioned in the preceding sections remain in place.

Use of Mole Fractions

We begin by introducing Eq. (2.5.7a) in the form $\mu_i(T, P) = \mu_i^*(T, 1) + RT \ln x_i$. Proceeding as in Section 2.9, the equilibrium condition in the present case is given by

$$0 = \left(\sum_i \nu_i \mu_i \right)_{eq} = \sum_i \nu_i \mu_i^*(T, 1) + RT \left(\sum_i \nu_i \ln x_i \right)_{eq}. \quad (2.10.1)$$

This leads us to introduce the corresponding equilibrium “constant” as

$$\ln K_x(T) \equiv - \sum_i \nu_i \mu_i^*(T, 1) / RT = \left(\sum_i \nu_i \ln x_i \right)_{eq}. \quad (2.10.2a)$$

Alternatively, we may write

$$K_x(T) = \prod_i (x_i^{\nu_i})_{eq}, \quad (2.10.2b)$$

whereby we have separated compositional terms on the right from quantities that depend parametrically on T .¹ Here the various $\mu_i^*(T, 1)$ represent the individual molar Gibbs free energies under standard conditions of 1 bar for all the constituents in pure form involved in the reaction. The above equation has the same form as Eq. (2.9.5a and b) but now there are no problems concerning units. However, you should note that if pressure units other than 1 bar were employed K_x would assume different values. You should study the requisite changes on your own.² By analogy to Eq. (2.9.10) we also find that

$$(\partial \ln K_x / \partial T)_{P=1} = \sum_i \nu_i \tilde{H}_i^*(T, 1) / RT^2 \equiv \Delta H_d^* / RT^2, \quad (2.10.3a)$$

where $\tilde{H}_i^*(T, 1)$ are individual molar enthalpies under standard conditions of 1 bar for all the constituents in pure form that are involved in the reaction. By similar methods, based on Section 2.9, we find that

$$(\partial \ln K_x / \partial P)_T = - \sum_i \nu_i \tilde{V}_i^*(T, 1) / RT \equiv - \Delta V_d^* / RT. \quad (2.10.3b)$$

By analogy with Eq. (2.9.8), we also write

$$\Delta G_d = -RT \ln K_x + RT \sum_i \nu_i \ln x_i = \Delta G_d^* + RT \sum_i \nu_i \ln x_i, \quad (2.10.4)$$

where $\Delta G_d^* = \sum_i \nu_i \mu_i^*(T, 1)$. The mole fractions on the right are those prevailing under non-equilibrium (arrested) conditions. As before, one must distinguish between values for mole fractions at

equilibrium, $(x_i)_{eq}$, and values (x_i) when a reaction is interrupted by use of constraints before equilibrium is reached.

Alternative formulations for the equilibrium constant and related quantities are found by introducing molarity, c_i , or molality, m_i , as concentration variables. This leads to rather messy relations that we really do not want to get into here. You can consult other sources³ for a detailed treatment.

Entropy Changes for Processes Totally within a System

We are finally able to complete the study of processes that occur totally within a system; we had alluded to this problem in Section 1.16. While the overall energy change in this case is zero, the entropy obviously changes. In general one can usually map any such process onto a chemical reaction, which then brings the machinery of Section 2.9 into play. It is easiest to visualize how to proceed by considering a generic example, such as the chemical change $2A + 3B = C$. In adopting this scheme we first set up the corresponding ΔG_d , and then deduce ΔS_d , which quantity may be integrated to find the desired entropy change for the process occurring in within the system.

The following tabulated example is used for orientation purposes: Starting with initial mole numbers n_A^0, n_B^0, n_C^0 , for the advancement of the reaction by $\lambda = n$ mole units, ($2n < n_A^0, 3n < n_B^0$) we find that

Reaction	2A	+	3B	=	C	
Current moles	$n_A^0 - 2n$		$n_B^0 - 3n$		$n_C^0 + n$	Total: $N^0 - 4n$ $N^0 \equiv n_A^0 + n_B^0 + n_C^0$
Mole fraction	$\frac{n_A^0 - 2n}{N^0 - 4n}$		$\frac{n_B^0 - 3n}{N^0 - 4n}$		$\frac{n_C^0 + n}{N^0 - 4n}$	

Then, according to Eq. (2.10.4),

$$dG = \left\{ \begin{array}{l} -RT \ln K_x(T, P) \\ +RT \left[\ln(n_C^0 + n) - 2 \ln(n_A^0 - 2n) - 3 \ln(n_B^0 - 3n) + 4 \ln(N^0 - 4n) \right] \end{array} \right\} dn, \quad (2.10.5a)$$

$\begin{matrix} I_1 & & -2I_2 & & -3I_3 & & +4I_4 \end{matrix}$

where the various I_j are defined as shown. In abbreviated form,

$$dG = \left[-RT \ln K_x(T, P) + RT \sum_{j=1}^4 \nu_j I_j \right] dn. \quad (2.10.5b)$$

We now determine the change in Gibbs free energy at constant T and P for a 1 mol change. A typical integral has the form $I = \int_0^1 \ln(a + bn)dn$. Introduce the change in variable $x = a + bn$. Then

$$I = (1/b) \int_a^{a+b} \ln x dx = (1/b) [(a+b) \ln(a+b) - a \ln a - b], \quad (2.10.6)$$

so that the change in Gibbs free energy for the indicated process reads

$$G_f - G_i = -RT \ln K_x(T, P) + RT \sum_{j=1}^4 \nu_j I_j, \quad (2.10.7)$$

where the following terms apply:

$$\begin{aligned} I_1 : a = n_C^0, b = 1, \nu = 1; \quad I_2 : a = n_B^0, b = -2, \nu = -2; \\ I_3 : a = n_C^0, b = -3, \nu = -3; \quad I_4 : a = N^0, b = -4, \nu = 4. \end{aligned}$$

We then obtain the entropy change in the customary manner:

$$S_f - S_i = R \ln K_x + \Delta H_d^0/T - R \sum_{j=1}^4 \nu_j I_j, \quad (2.10.8)$$

which achieves the goal we set out, namely, to specify the entropy change for any process that occurs totally within a system when the release of a constraint initiates the change.

General Discussion

We complete the discussions by noting the following. Considering

$$K_x = \exp[-\Delta G_d^*(T, 1)/RT], \quad (2.10.9)$$

if K_x is to be very large and positive then ΔG_d^* must be a very large negative quantity; hence, the reaction as written will proceed spontaneously nearly to completion; in the final equilibrium state one ends up with a preponderance of products over reagents. Conversely, for very small values of the equilibrium constants ΔG_d^* will be a large positive quantity, so that the reaction proceeds spontaneously in the direction opposite to that which is written down. At quiescence reagents will then predominate over products. Equilibrium constants in the neighborhood of unity indicate an equilibration of reagents and products at comparable mole numbers. Finally, it should be obvious that the equilibrium constants are not unique; they depend on the choice of pressures and are functions of temperature; only the ratios $\Delta G_d(T)/RT$ are unique.

Comments

- 2.10.1.** To avoid excessive repetition we remind the reader to set $P = 1$ bar whenever standard conditions are called for. See also the end of the present section.
- 2.10.2.** Derive relations that show how K_x would be altered if pressure units other than bars were adopted. Hint: Show that the pressure variation of K_x involves the molar volumes, and then introduce the isothermal compressibilities.
- 2.10.3.** See, e.g., J.M. Honig *Thermodynamics*, 3rd Ed. (Academic Press, Amsterdam, 2007), Section 2.10.

2.11 Chemical Equilibrium in Ideal Heterogeneous Systems

We now briefly consider systems in which one or more pure condensed phases coexist with an ideal homogeneous mixture in liquid or solid form. It is then expedient to distinguish between pure

condensed phases, subscript s , and species involved in the solution, subscript i . For the reaction, written as $\sum_s \nu_s A_s + \sum_i \nu_i A_i = 0$ we write out the equilibrium condition as

$$\Delta G_d = \sum_s \nu_s \mu_s^* + \left(\sum_i \nu_i \mu_i \right)_{eq} = 0, \quad (2.11.1)$$

which forms the basis of our subsequent discussion.

Equilibrium with Ideal Gases

Here we apply Eq. (2.4.15) to Eq. (2.11.1) to write

$$\sum_i \nu_i \mu_i^{OP}(T) + \sum_s \nu_s \mu_s^*(T, 1) + RT \left(\sum_i \nu_i \ln P_i \right)_{eq} = 0. \quad (2.11.2)$$

where we reference the chemical potentials of the pure condensed phase to those under standard conditions of 1 bar. Once again, we separate pressure variables pertaining to the gaseous mixture from the remainder. This generates an equilibrium constant via

$$\ln K_P \equiv - (1/RT) \left[\sum_i \nu_i \mu_i^{OP}(T) + \sum_s \nu_s \mu_s^*(T, 1) \right], \quad (2.11.3)$$

so that

$$\ln K_P = \left(\sum_i \nu_i \ln P_i \right)_{eq}, \quad \text{or} \quad K_P(T, 1) = \prod_i (P_i^{\nu_i})_{eq}, \quad (2.11.4)$$

wherein the quantities referring to the pure phases are absent. In some sources one finds statements to the effect that the pure condensed phases are considered as being at “unit activity”, whence there is no reference to the s species in Eq (2.11.4). In fact, this situation arises because of the separation of variables into terms that do and do not involve the composition of the solution.

The equilibrium “constant” varies with temperature according to the relation

$$\left(\frac{\partial \ln K_P}{\partial T} \right)_P = \frac{\sum_i \nu_i \bar{H}_i^*(T, 1) + \sum_s \nu_s \bar{H}_s^*(T, 1)}{RT^2} \equiv \frac{\Delta H_d^*}{RT^2}. \quad (2.11.5)$$

Lastly, we may specify the differential Gibbs free energy change as follows:

$$\begin{aligned} \Delta G_d &= \sum_i \nu_i \mu_i^{OP}(T) + \sum_s \nu_s \mu_s^*(T, 1) + RT \sum_i \nu_i \ln P_i \\ &= \Delta G_d^{OP} + RT \sum_i \nu_i \ln P_i \\ &= -RT \ln K_P + RT \sum_i \nu_i \ln P_i. \end{aligned} \quad (2.11.6)$$

As the notation implies, the partial pressures in Eq. (2.11.6) refer to conditions away from equilibrium. At equilibrium ΔG_d vanishes.

Ideal Solutions in Equilibrium with Pure Condensed Phases

We use the same strategy here as in the preceding section in terms of the mole fractions x_i for units forming the condensed solution. Relative to the standard state we characterize the equilibrium condition by

$$\begin{aligned}\Delta G_d &= \sum_i \nu_i \mu_i^*(T, 1) + \sum_s \nu_s \mu_s^*(T, 1) + RT \sum_i (\nu_i \ln x_i)_{eq} \\ &= \Delta G_d^* + RT \sum_i (\nu_i \ln x_i)_{eq} = 0.\end{aligned}\quad (2.11.7)$$

Once more, s refers to liquids or solids in pure form, i , to constituents in the solution. We separate out terms that do not depend on the solution composition from those that do, thereby introducing the equilibrium constant

$$\ln K_x \equiv - (1/RT) \left[\sum_s \nu_s \mu_s^*(T, 1) + \sum_i \nu_i \mu_i^*(T, 1) \right] = -\Delta G_d^*/RT, \quad (2.11.8)$$

so that

$$\ln K_x = \sum_i (\nu_i \ln x_i)_{eq} \quad \text{or} \quad K_x = \prod_i (x_i^{\nu_i})_{eq}. \quad (2.11.9)$$

Again, only species in solution make their appearance on the right. The remainder of the analysis proceeds as before. In particular, we obtain

$$\left(\frac{\partial \ln K_x}{\partial T} \right)_{P=1} = \frac{\sum_i \nu_i \bar{H}_i^*(T, 1) + \sum_s \nu_s \bar{H}_s^*(T, 1)}{RT^2} \equiv \frac{\Delta H_d^*}{RT^2}. \quad (2.11.10)$$

It should also be evident that

$$\left(\frac{\partial \ln K_x}{\partial P} \right)_T = - \frac{\sum_i \nu_i \tilde{V}_i^*(T, 1) + \sum_s \nu_s \tilde{V}_s^*(T, 1)}{RT} \equiv \frac{\Delta V_d^*}{RT} \quad (2.11.11)$$

2.12 Equilibrium between Two Ideal Phases

Consider a given species i distributed between two phases $'$ and $''$ at equilibrium, one of which is a gas phase. Equality of the chemical potential leads to the expression

$$\mu_i^{OP}(T) + RT \ln P_i'' = \mu_i^*(T, P) + RT \ln x_i' \quad (2.12.1)$$

for the equilibration of i in the gas and in condensed phase. Six additional interrelations could be presented in which the composition of the condensed phase is specified as molarity or molality, but these are not presented here. Based on the above one can obviously introduce equilibrium constants such as $K_{px} \equiv - [\mu_i^{OP}(T) - \mu_i^*(T, 1)]/RT$, so that one can rewrite the equilibrium constraints in the form

$$K_{px} = P_i''/x_i' \quad (2.12.2)$$

where equilibrium values of P_i and x_i are to be specified. The above relation is simply a reformulation of Raoult' law as applied to the solvent.

Characterization of Nonideal Solutions

3

3.0 Introductory Remarks

So far we have considered an idealized version of thermodynamics. However, real life is never this tidy. To deal with reality requires an adaptation of Chapter 2; we must take account of interactions between species that have been ignored so far. These are responsible for deviations from ideality, and can never be “turned off”. In the thermodynamic characterization of nonideal solutions, we adopt two guiding principles: (i) The formulations presented in Chapters 1 and 2 are so convenient that it is worth preserving their *form* when characterizing nonideal systems. (ii) When systems approach ideal behavior, the present analysis must correctly reduce to that of Chapter 2; in particular, for gases at low pressure and high temperature, and for very dilute solutions.

3.1 Thermodynamic Treatment of Nonideal Gas Mixtures

Nonideal Gaseous Mixtures

Equation (2.4.15) relates the chemical potential of an ideal gas to $RT \ln P_i$; in accordance with (i), this suggests that μ_i for a real gas should be specified by an analogous expression, namely $RT \ln f_i$, where f is termed the *fugacity* of the i th constituent of the gas. To satisfy (ii), this quantity must converge on the pressure P_i at ideality. Since μ_i is specified only to within an arbitrary constant, only the difference in chemical potential of the nonideal gas in two states, 1 and 2, may be uniquely specified as

$$\mu_i(T, f_2) - \mu_i(T, f_1) = RT \ln f_2 - RT \ln f_1. \quad (3.1.1)$$

Now let 1 represents a specifically chosen *reference state* in which the gas has fugacity f_i^0 and let 2 represents any other experimental state of the gaseous system, with fugacity f_i . Then Eq. (3.1.1) may be rewritten as

$$\mu_i(T, f_i) = \mu_i(T, f_i^0) + RT \ln(f_i/f_i^0). \quad (3.1.2)$$

This relation is self-consistent, reducing to an identity for $f_i = f_i^0$. It is customary to choose as *the reference state the gas species i in ideal form*; that is, we select $f_i^0 = P_i$, and we then adopt Eq. (2.4.15):

$$\mu_i(T, f_i^0) = \mu_i^{OP}(T) + RT \ln P_i. \quad (3.1.3)$$

When Eq. (3.1.3) is substituted in Eq. (3.1.2), one obtains the *canonical form*

$$\mu_i(T, f_i) = \mu_i^{OP}(T) + RT \ln f_i, \quad (3.1.4a)$$

which properly reduces to the ideal gas case wherein all gas interactions are turned off. The fact that such a state cannot actually be realized—only approached—should act as no deterrent, so long as that same reference state (which, in any event, is completely arbitrary) is always retained.

To emphasize deviations from ideality, we introduce the so-called *activity coefficient* or *fugacity coefficient* defined by $\gamma_i \equiv f_i/P_i$ and rewrite Eq. (3.1.4a) in the form

$$\mu_i(T, f_i) = \mu_i^{OP}(T) + RT \ln \gamma_i + RT \ln P_i. \quad (3.1.4b)$$

Then $\mu_i^{OP}(T)$ is the standard chemical potential for species i when $\gamma_i = 1$ and when $P_i = 1$ bar.¹ Clearly, we require that in the limit $P \rightarrow 0$, $\gamma_i \rightarrow 1$, so that $f_i \rightarrow P_i$.

Experimental Determination of Fugacities

The above analysis is all well and good, but it is purely formal until one establishes how fugacities may be determined experimentally. Here we cite one particular technique for this purpose.

Starting with the relation $d\mu_i = RT d \ln f_i$, at a fixed temperature T , we obtain for constant composition x_i of the gas phase,

$$\left(\frac{\partial \ln f_i}{\partial P} \right)_{T, x_i} = \left(\frac{\partial \mu_i}{\partial P} \right)_{T, x_i} = \frac{\bar{V}_i}{RT}. \quad (3.1.5)$$

Note that we are invoking here the total pressure variation, since only this quantity can be readily measured, and because it is the total pressure that dictates deviations from ideality. Next, introduce a term

$$b_i \equiv \bar{V}_i - RT/P \quad (3.1.6)$$

that measures deviations of the actual gas from ideal gas behavior. Then

$$d \ln f_i|_{T, x_i} = \left(\frac{b_i}{RT} + \frac{1}{P} \right) dP = \frac{b_i}{RT} dP + d \ln P, \quad (3.1.7)$$

or, on integrating,

$$\int_{P_l}^P d \ln(f_i/p) = (1/RT) \int_{P_l}^P b_i dp = \ln(f_i/P) - \ln(f_{il}/P_l), \quad (3.1.8)$$

at constant T, x_i . Here P_l represents some very low total pressure, where the fugacity is sensibly equal to the partial pressure of the gas, so that we can set $f_{il} = x_i \cdot P_l$. Then,

$$\ln(f_i/P) = (1/RT) \int_{P_l}^P b_i dp + \ln x_i \quad (T, x_i \text{ constant}). \quad (3.1.9)$$

In principle, this equation may be used to find the fugacity of i in the gas mixture once the dependence of b_i on P has been empirically established.

Fugacity of a Pure Gas

For purposes of illustration, we now consider a one-component gas for which $b = \tilde{V} - RT/P$. It is simplest to integrate Eq. (3.1.5) directly to find

$$\ln\left(\frac{f}{P_l}\right) = \frac{1}{RT} \int_{P_l}^P \tilde{V}(T, p) dp. \quad (3.1.10)$$

In principle, this accomplishes the task: one measures the (molar) volume of the nonideal gas as a function of the applied pressure at fixed temperature T , beginning at a very low, fixed value of the pressure, P_l , and ending at the pressure P for which the fugacity f is to be found. At that low value, the fugacity and the actual gas pressure are essentially identical. Clearly, this is not a very satisfactory way of dealing with the lower limit. Additionally, Eq. (3.1.10) is limited in use to purely empirical observations.

As an alternative, one may employ an equation of state; this leads to a rather lengthy but instructive excursion. The difficulty here is that the equation of state is usually specified in the form $P = P(T, V)$, which cannot readily be inverted for use in Eq. (3.1.10). We therefore begin by citing Eq. (1.12.18), valid at a fixed temperature T :

$$E(T, V) = E^*(T) + \lim_{v \rightarrow \infty} \int_v^V [T(\partial P / \partial T)_V - P] dv. \quad (3.1.11)$$

By way of illustration, we first consider relations based on the Berthelot equation of state (1907) for a gas consisting of n moles:

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{TV^2}, \quad (3.1.12)$$

where a and b are the empirical constants, independent of T and V . For this case, the integration of Eq. (3.1.11) yields

$$E(T, V) = \left(\frac{3}{2}\right)nRT - \frac{2n^2 a}{VT} = \left(\frac{3}{2}\right)nRT \left[1 - \frac{4na}{3VRT^2}\right]. \quad (3.1.13)$$

Ordinarily the correction term does not exceed unity by more than 10%.

The determination of the entropy for real gases requires care. The starting relation for the entropy at (T_2, P_2) relative to (T_1, P_1) reads

$$S(T_2, P_2) = S(T_1, P_1) + \int_{T_1}^{T_2} \frac{C_P(T, P_1)}{T} dT - \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP. \quad (3.1.14a)$$

As usual, the entropy needs to be referred to the entropy of an ideal gas, for which purpose one must choose a very low pressure, $P_1 = P_l$, which is then allowed to approach zero. In this limit, we set $S(T_1, P_1) = S^*(T_1, P_l)$ and $C_P(T, P_1) = C_P^*(T, P_l)$, where the asterisks here refer to the properties

of the ideal gas. A problem that now arises occurs in the second integral which diverges at the lower limit; as a remedy, we rewrite the above in the form

$$S(T_2, P_2) = S^*(T_1, P_l) + \int_{T_1}^{T_2} \frac{C_P^*(T, P_l)}{T} dT - \int_{P_l}^{P_2} \left[\left(\frac{\partial V}{\partial T} \right)_P - \frac{nR}{P} \right] dP - \int_{P_l}^{P_2} \frac{nR}{P} dP, \quad (3.1.14b)$$

where the compensating terms were inserted so that in the second integral, one may set $P_l \rightarrow 0$, where $(\partial V/\partial T)_P \rightarrow nR/P_l$. Then, this central integral no longer diverges at its lower limit; instead, the problem is shifted to the third integral.

To handle this situation, we relate the total entropy to that of the ideal gas at constant temperature and at a standard pressure $P_l = P_0 = 1$ bar, $S^*(T_2, P_0)$. According to Eq. (2.4.10), we set

$$S^*(T, P_l) \equiv S^*(T, P_0) + [S^*(T, P_l) - S^*(T, P_0)] = S^*(T, P_0) - nR \ln P_l, \quad (3.1.15)$$

and notice that the last term cancels against the lower limit of the third integral. For the special case $T_2 = T_1$, the substitution of Eq. (3.1.15) into Eq. (3.1.14b) then leaves

$$S(T, P) = S^*(T, P_0) - \int_0^P \left[\left(\frac{\partial V}{\partial T} \right)_P - \frac{nR}{P} \right] dP - nR \ln P. \quad (3.1.16)$$

For the determination of the partial derivative, we again introduce the Berthelot gas: one finds on integration that

$$S(T, P) = S^*(T, P_0) + [(2b/T) + (3na/RT^3)]P - nR \ln P. \quad (3.1.17)$$

One may then add Eqs. (3.1.11) and (3.1.16)—multiplied by T —to determine the Gibbs free energy, set $n = 1$, and use Eq. (3.1.4a) to find the fugacity. The execution of these steps for the Berthelot gas is left for you as an exercise.

Notes and Exercise

- 3.1.1.** If one wishes to adopt a chemical potential reference standard that is experimentally accessible, one could return to Eq. (3.1.4a), set $f_i^o = 1$ to obtain $\mu_i(T, f_i) = \mu_i(T, 1) + RT \ln f_i$. This reference value differs from that in Eqs. (3.1.4), and leads to different fugacity scales. For better or for worse, the ideal gas state is usually adopted as the standard, because criterion (ii) is then satisfied.
- 3.1.2.** Determine the chemical potential, hence, the fugacity of the Berthelot gas.

3.2 Temperature and Pressure Dependence of the Fugacity of a Gas

The temperature dependence of the fugacity is found by rewriting Eq. (3.1.4b) for a one-component system in the form

$$\ln \gamma = [\mu(T, P) - \mu^{OP}(T)]/RT - \ln P, \quad (3.2.1)$$

so that, using Eq. (2.5.3),

$$\left(\frac{\partial \ln \gamma}{\partial T}\right)_P = -\frac{\tilde{H}(T, P) - \tilde{H}^0(T)}{RT^2} = \left(\frac{\partial \ln f}{\partial T}\right)_P. \quad (3.2.2)$$

The right-hand side obtains because at fixed P, f and $\gamma = f/P$ change in the same manner with T . The quantity to be specified above is the enthalpy of the ideal gas, $\tilde{H}^0(T) = (5/2)RT$. Alternatively, we note that at very low pressures, $\mu(T, P_l) = \mu^{OP}(T) + RT \ln P_l$. Then,

$$\mu(T, f) - \mu(T, P_l) = RT \ln P - RT \ln P_l + RT \ln \gamma, \quad (3.2.3)$$

so that

$$\left(\frac{\partial \ln \gamma}{\partial T}\right)_{P, P_l} = -\frac{\tilde{H}(T, P) - \tilde{H}(T, P_l)}{RT^2} = \left(\frac{\partial \ln f}{\partial T}\right)_{P, P_l}. \quad (3.2.4)$$

Here we relate the temperature variations to the enthalpy difference of the actual gas at pressure P and at a very low pressure P_l . This difference may be evaluated, for example, by integrating the caloric equation of state, Eq. (1.12.10b).

The pressure variation is found from Eq. (3.2.1) by writing

$$(\partial \ln \gamma / \partial P)_T = (1/RT)(\partial \mu / \partial P)_T - 1/P = \tilde{V}/RT - 1/P. \quad (3.2.5)$$

On the other hand, from $\gamma = f/P$, we obtain

$$(\partial \ln \gamma / \partial P)_T = (\partial \ln f / \partial P)_T - 1/P, \quad (3.2.6)$$

so that

$$(\partial \ln f / \partial P)_T = \tilde{V}(T, P)/RT, \quad (3.2.7)$$

requiring the specification of the equation of state of the real gas, or a measurement of the actual molar volume, followed by the integration that yields the dependence of f on P .

3.3 Thermodynamic Description of Real Solutions in the Condensed State

Thermodynamic Functions for Pure Condensed Phases

We now shift attention to the thermodynamic characterization of actual condensed material in pure form. Introduce the equation of state that specifies the volume as a function of temperature and pressure as

$$V = V_0(1 + \alpha_1 T + \alpha_2 T^2 - \beta_1 P - \beta_2 PT), \quad (3.3.1)$$

where V_0 is the volume of the solid or liquid at *some standard value* and the various coefficients are positive constants that must be determined empirically. In many applications, the terms in T^2 and TP are omitted.

The enthalpy at a fixed temperature is found by use of Eq. (1.12.19b); relative to standard conditions, with $P_1 = P^* = 1$ bar, one sets

$$\begin{aligned} H(T, P) &= H(T, P_0) + \int_{P_0}^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP \\ &= H(T, P_0) + V_0(P - P_0) \left[1 - \alpha_2 T^2 - \beta_1(P + P_0)/2 \right]. \end{aligned} \quad (3.3.2)$$

The entropy relative to its standard value at fixed temperature T is specified by invoking the appropriate Maxwell relation:

$$\begin{aligned} S(T, P) &= S(T, P_0) - \int_{P_0}^P \left(\frac{\partial V}{\partial T} \right)_P dP \\ &= S(T, P_0) - V_0(P - P_0) [\alpha_1 + 2\alpha_2 T - \beta_2(P + P_0)/2]. \end{aligned} \quad (3.3.3)$$

If desired, one may refer the entropy to 0 K by setting $P_0 = 0$.

The Gibbs free energy is specified by addition of Eqs. (3.3.2) and (3.3.3):

$$G(T, P) = G(T, P_0) + V_0(P - P_0) \left[1 - \alpha_1 T - 3\alpha_2 T^2 - (P + P_0)(\beta_1 - \beta_2 T)/2 \right]. \quad (3.3.4)$$

By changing over to molar values of G and of V , you obtain the chemical potential of the condensed phase in terms of the relevant equation of state. In general, the correction terms in square brackets are small compared to unity, and those involving α_2 and β_2 are frequently omitted.

Thermodynamic Properties of Solutions of Condensed Phases

We next consider the chemical potential of components forming nonideal solutions in the condensed state. This is based on the canonical formulation of ideal solutions, introduced in Section 2.5,

$$\mu_i(T, P, x_i) = \mu_i^*(T, P) + RT \ln x_i, \quad (3.3.5)$$

where $\mu_i^*(T, P)$ is the (temporary) reference value of the chemical potential of species i in its pure state at the prevailing temperature T and pressure P . Standard operating procedures call for the preservation of the above formulation for nonideal solutions. This is done by introducing *activities* a_i such that for actual solutions, an equation of the *canonical form*

$$\mu_i(T, P, x_i) = \mu_i^*(T, P) + RT \ln a_i(T, P, x_i) \quad (3.3.6)$$

is applicable. As indicated, the quantity a_i generally depends on temperature, pressure, and composition, so as to take into account the interactions between species in solution that were neglected in Chapter 2. Again, the above relation is purely formal until one can relate the activities to measured mole fractions. We shall deal with this problem below.

The above equation is self-consistent in that at unit activity, characteristic of pure materials, one obtains an identity. However, the reference value of the chemical potential chosen above is not unique.

It is thus expedient to relate $\mu_i(T, P, x_i)$ to the chemical potential of pure i at the standard pressure $P_0 = 1$ bar. We amend Eq. (3.3.6) to read

$$\mu_i(T, P, x_i) = \mu_i(T, 1, 1) + RT \ln[a_i(T, P, x_i)/a_i(T, 1, 1)], \quad (3.3.7)$$

which also reduces to an identity for $P = 1$ and $x_i = 1$. Here $\mu_i(T, 1, 1) = \mu_i^*(T, 1)$ represents the chemical potential for pure i at $P = 1$ bar. Clearly, in conformity with Raoult's Law, ideal behavior obtains when $x_i \rightarrow 1$, so that we may set $a_i(T, 1, 1) = x_i^* = 1$, whence we obtain the *canonical form*

$$\mu_i(T, P, x_i) = \mu_i^*(T, 1) + RT \ln a_i(T, P, x_i). \quad (3.3.8)$$

Here we have circumvented the problem of self-consistency that was raised in conjunction with Eq. (2.5.7b), because activities are pressure-dependent.

It is customary to rewrite the above relation by introducing an *activity coefficient* $\Gamma_i(T, P, x_i) = a_i(T, P, x_i)/x_i$ so as to write

$$\mu_i(T, P, x_i) = \mu_i^*(T, 1) + RT \ln x_i + RT \ln \Gamma_i(T, P, x_i). \quad (3.3.9)$$

Note that $\Gamma_i(T, 1, 1) = 1$. However, as shown later, even for pure materials at pressures other than 1 bar, $\Gamma_i(T, P, 1)$ and $a_i(T, P, 1)$ deviate from unity. This reflects the fact that a compressed material experiences greater interactions among its constituent particles than one at lesser compression. Thus, even at constant composition, the activities of every species, both in the pure state and in solution, do vary with pressure, as does $\Gamma_i(T, P, x_i)$.

If concentration units other than mole fractions are chosen, one encounters a much more cumbersome set of interrelations. If interested in this problem, please refer to a detailed exposition provided elsewhere.²

Query and Reference

- 3.3.1.** There appears to be a problem with dimensional analysis in Eq. (3.3.2), where α_1 and β_2 are constants. Resolve this apparent problem. Hint: α_1 represents the isobaric expansion coefficient.
- 3.3.2.** See, for example, J.M. Honig, *Thermodynamics* (Academic Press, Amsterdam, 2007), 3rd Ed., Sections 3.3–3.6.

3.4 Characterization of Chemical Equilibrium in Nonideal Solutions

General Approach

To characterize equilibrium conditions for reactions in a nonideal solution, we start with the criterion for chemical equilibrium, $(\sum_l \nu_l \mu_l)_{eq} = 0$, developed in Sections 2.9–2.11. Here again the ν_l indicates the stoichiometry coefficients for the generalized chemical reaction $\sum_l \nu_l A_l = 0$, where the A_l represents all of the participating species; ν_l is positive or negative accordingly as the corresponding A_l represents a product or a reagent for the reaction as written. Although many different strategies are

available, the most straightforward approach involves use of Eq. (3.3.8) or Eq. (3.3.9) as the starting point. As developed in Chapter 2, the equilibrium state is therefore characterized by

$$\sum_l v_l \mu_l(T, 1, 1) + \sum_l v_l RT \ln[a_l(T, P, x_l)]_{eq} = 0, \quad (3.4.1)$$

which leads to the construction of an equilibrium “constant” of the form

$$\ln \mathcal{K}(T, 1) \equiv - (RT)^{-1} \sum_l v_l \mu_l^*(T, 1) = \sum_l v_l \ln[a_l(T, P, x_l)]_{eq}, \quad (3.4.2a)$$

$$\mathcal{K}(T, 1) = \prod_l [a_l(T, P, x_l)]_{eq}^{v_l}. \quad (3.4.2b)$$

Note that $\mathcal{K}(T, 1)$ here is defined by the chemical potentials of all species in their standard state of 1 bar.

One is at liberty to distinguish between pure condensed phases indexed by s and the species constituting the solution, j (such as ice in equilibrium with a sugar solution). On rewriting Eq. (3.4.1) according to this pattern, one finds

$$\begin{aligned} (-RT)^{-1} \left[\sum_s v_s \mu_s^*(T, 1) + \sum_j v_j \mu_j^*(T, 1) \right] \\ \equiv \ln \mathcal{K}_x(T, 1) = \sum_s v_s \ln a_s(T, P, 1) + \sum_j v_j \ln a_j(T, P, x_j) \Big|_{eq} \end{aligned} \quad (3.4.3)$$

$$\mathcal{K}_x(T, 1) = \prod_s a_s(T, P, 1)^{v_s} \prod_j a_j(T, P, x_j) \Big|_{eq}^{v_j}. \quad (3.4.4)$$

This has the advantage of separating out the terms that depend on composition from those that do not. We show below that the activities indexed by s usually do not deviate significantly from unity, whence the principal variable factors in the equilibrium constants are the activities for the intermingled species in solution.

Free-Energy Changes

An alternative, equivalent point of view derives from the interrelation between ΔG_d and $\ln \mathcal{K}_x$. On writing $\Delta G_d = \sum_l v_l \mu_l$ and utilizing Eqs. (2.10.4) and (3.4.2a), one finds

$$\Delta G_d = \sum_l v_l \mu_l^*(T, 1) + RT \sum_l v_l \ln a_l(T, P, x_l) \quad (3.4.5a)$$

$$= -RT \ln \mathcal{K}_x(T, 1) + RT \sum_l v_l \ln a_l(T, P, x_l) \quad (3.4.5b)$$

$$= -RT \sum_l v_l \ln[a_l(T, P, x_l)]_{eq} + RT \sum_l v_l \ln a_l(T, P, x_l). \quad (3.4.5c)$$

On introducing the definition $\sum_l v_l \mu_l^*(T, 1) \equiv \Delta G_d^{0*}$ into Eq. (3.4.2a), one obtains the important relation

$$\ln \mathcal{K} = -\Delta G_d^{0*} / RT. \quad (3.4.6)$$

The definition shows that ΔG_d^{0*} is the differential Gibbs free energy per unit advancement of the reaction $\sum_l v_l A_l = 0$ when all components are in their pure state under standard (unit) pressure. That

such a system may not be experimentally accessible is not of concern since one can simply look up tabulated values of $\mu_l^*(T, 1)$ or use the results of Section 3.3 for all the pure components, and thereby obtain ΔG_d^{0*} . Using Eq. (3.4.6), Eq. (3.4.5b) becomes

$$\Delta G_d = \Delta G_d^{0*} + RT \sum_l \nu_l \ln a_l(T, P, x_l). \quad (3.4.7)$$

It is important to recognize that the last term in Eqs. (3.4.5) and (3.4.7) specifies activities under conditions other than equilibrium, i.e., when the system is constrained to remain in a different quiescent state (Section 2.9). We return to Eqs. (3.4.5) to note the fundamental interrelation between (i) the Gibbs free-energy change per unit advancement of the reaction, as specified by $\sum_l \nu_l A_l = 0$, when all participating species are isolated and maintained at standard conditions, and (ii) the natural logarithm of the equilibrium constant pertaining to the reaction in question.

If one distinguishes between pure condensed phases (*s*) and homogeneous mixtures (*i*), one obtains the relations

$$\begin{aligned} \Delta G_d &= \sum_s \nu_s \mu_s + \sum_j \nu_j \mu_j \\ &= \sum_s \nu_s \mu_s^*(T, 1) + \sum_j \nu_j \mu_j^*(T, 1) + RT \sum_s \nu_s \ln a_s(T, P, 1) + RT \sum_j \nu_j \ln a_j(T, P, x_j) \\ &= -RT \ln \mathcal{K}_x(T, 1) + RT \sum_s \nu_s \ln a_s(T, P, 1) + RT \sum_j \nu_j \ln a_j(T, P, x_j). \end{aligned} \quad (3.4.8)$$

On setting $\Delta G_d^{os} \equiv \sum_s \nu_s \mu_s^*(T, 1) + \sum_j \nu_j \mu_j^*(T, 1)$, one obtains an analog of Eq. (3.4.6), namely,

$$\ln \mathcal{K}_x(T, 1) = -\Delta G_d^{os} / RT, \quad (3.4.9)$$

so that Eq. (3.4.9) may be rewritten as

$$\Delta G_d = \Delta G_d^{os} + RT \sum_s \nu_s \ln a_s(T, P, 1) + RT \sum_j \nu_j \ln a_j(T, P, x_j). \quad (3.4.10)$$

Note the trivial distinction between ΔG_d^{os} and ΔG_d^{0*} .

Pressure and Temperature Variations of the Equilibrium Parameter

The definitions of the equilibrium parameters for nonideal systems involve the chemical potentials of the pure constituents that undergo the reaction of interest. Thus, they are the same as those adopted for ideal systems. For this reason, the methodology and the results of Section 2.10 may be taken over (with appropriate minor notational modifications, as necessary) and need not be repeated here.

There remains the minor discrepancy of having the left-hand side of equations such as Eqs. (3.4.2) or Eq. (3.4.4) specified in terms of unit pressure, while the right-hand side involves an arbitrary pressure *P*. This is a direct consequence of the original choice of the standard state to which the chemical potentials have been referred. This occasions no problems since the properties of materials in their standard state can always be obtained empirically or are provided in tabulations.

Equilibrium Constants, General Discussion

The equilibrium constants may be rewritten in the form

$$\begin{aligned} K_x(T, 1) &= \prod_s [a_s(T, P, 1)]^{\nu_s} \prod_j [a_j(T, P, x_j)]_{eq}^{\nu_j} \\ &= \left\{ \prod_s [\Gamma_s(T, P, 1)]^{\nu_s} \prod_j [\Gamma_j(T, P, x_j)]_{eq}^{\nu_j} \right\} \prod_j x_j|_{eq}^{\nu_j}. \end{aligned} \quad (3.4.11)$$

As in the case of ideal solutions, the equilibrium constant involves a ratio of factors for the equilibrium concentration variables x_j , raised to the appropriate power. This ratio is now preceded by two factors, enclosed in curly brackets, that attend to the nonideality of the participants in the chemical reaction. Departures from ideality of the unmixed components (first factor) are discussed immediately below; under normal conditions, the corresponding activity coefficients do not differ greatly from unity. For the intermixed components, one must look up in appropriate tabulations values of the various activity coefficients $\Gamma_j(T, P, x_j)$. Methods for their experimental determination are also introduced below.

Activities and Equilibrium Constants for Pure Condensed Phases

We here determine the activity coefficients for the undissolved species that are customarily omitted from the right-hand side of Eq. (3.4.11). This step is frequently summarized by the statement that “the activity of all pure condensed phases is unity,” whence these factors drop out. The degree to which this claim is tenable is examined below.

Toward this goal, we consider the chemical potential in differential form for a pure condensed phase: $d\mu_s|_T = \tilde{V}_s dP|_T = RT d \ln a_s(T, P, 1)|_T$. On integrating from $P = 1$ to the pressure of interest, we find

$$\ln[a_s(T, P, 1)] - \ln[a_s(T, 1, 1)] = (1/RT) \int_1^P \tilde{V}_s^*(T, p) dp. \quad (3.4.12)$$

For modest changes from atmospheric pressure, the molar volume for condensed phases, \tilde{V}_s , changes very little with pressure, so that it may be regarded as sensibly constant. Furthermore, as stated earlier, $a_s(T, 1, 1) = 1$. Then Eq. (3.4.12) becomes

$$\ln \Gamma_s(T, P, 1) = \ln[a_s(T, P, 1)] \approx \frac{(P-1)\tilde{V}(T, 1, 1)}{RT}. \quad (3.4.13)$$

Ordinarily, the ratio on the right-hand side is quite small, especially if the total pressure does not deviate greatly from unity. In that event, the right-hand side nearly vanishes; then, taking anti-logarithms, leads to the result

$$\Gamma_s(T, P, 1) = a_s(T, P, 1) \approx 1, \quad (3.4.14)$$

so that deviations from ideality indeed tend to be small. In particular, $\Gamma_s(T, 1, 1)a_s(T, 1, 1) = 1$, i.e., *the activity coefficient Γ_s and activity of all pure condensed phases is unity under standard conditions $P = 1$ bar*. Therefore, activities of the species in their pure state are frequently omitted from further consideration.

The corresponding determination of activity products for species in a mixture is more involved and will be considered later.

For gaseous species, the simplest procedure is to substitute fugacities in place of activities. This brings the machinery of Section 3.1 to bear on the problem. Formally, one may adhere more closely to the methodology of the present section by writing $f_i \equiv P_i(f_i/P_i) \equiv \Gamma_i^g(T, P, P_i)P_i$. The quantities $\Gamma_i^g(T, P, P_i) = f_i(T, P, P_i)/P$ are specified as shown in Section 3.1.

Caveat

An important function of the equilibrium parameter relates to the fact that the various concentrations or activities of species maintained at equilibrium obviously are not independent. Every chemical reaction or equilibration introduces one interrelation between the interacting species. Hence, the number of independent composition variables in a system is reduced by one for every equilibrium relation in a given experimental situation.

Representative Examples Pertaining to Equilibrium

It may not be out of place to present representative examples that illustrate some general features of equilibrium configurations.

Dissociation of Water Vapor

In this calculation, we neglect the deviation of the vapor phase constituents from ideality. Let α represents the degree of dissociation of water into its elements. Then the following scheme may be devised for the study of equilibration conditions:

Equation	$2\text{H}_2\text{O}(\text{g})$	=	$2\text{H}_2(\text{g})$	+	$\text{O}_2(\text{g})$	
Relative mole numbers	$1 - \alpha$		α		$\alpha/2$	Total: $1 + \alpha/2$
Mole fractions	$\frac{1 - \alpha}{1 + \alpha/2}$		$\frac{\alpha}{1 + \alpha/2}$		$\frac{\alpha/2}{1 + \alpha/2}$	
Partial pressures	$\frac{1 - \alpha}{1 + \alpha/2} P$		$\frac{\alpha}{1 + \alpha/2} P$		$\frac{\alpha/2}{1 + \alpha/2} P$	
Concentration	$\frac{1 - \alpha}{V}$		$\frac{\alpha}{V}$		$\frac{\alpha/2}{V}$	

Here P is the total pressure of the gas phase. The equilibrium “constant” for the reaction as written is given by

$$K_x = \frac{\alpha^3}{2(1 - \alpha)^2(1 + \alpha/2)} \quad (3.4.15a)$$

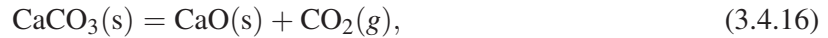
$$K_P = \frac{P_{\text{H}_2}^2 P_{\text{O}_2}}{P_{\text{H}_2\text{O}}^2} = \frac{\alpha^3 P}{2(1 - \alpha)^2(1 + \alpha/2)} \quad (3.4.15b)$$

$$K_c = \frac{\alpha^3}{2(1 - \alpha)^2 V} \quad (3.4.15c)$$

Experimental work shows that at $P = 1$ bar, $\alpha = 5.04 \times 10^{-3}$ and 1.21×10^{-2} at $T = 2000, 2200$ K. Insertion into Eq. (3.4.1) yields $K_P = 6.45 \times 10^{-8}, 9.02 \times 10^{-7}$ bar at those two temperatures. Thus, the degree of dissociation is very tiny even at these elevated temperatures; the small value of K_P likewise shows that in the reaction as written, the “reagent” heavily outweighs the “products” at equilibrium. Once K_P has been determined, one can calculate the average enthalpy of dissociation close to 2100 K, associated with the equilibrium state, according to the relation $\Delta H_d^0 = [RT_1 T_2 / (T_2 - T_1)] \ln[K_P(T_2)/K_P(T_1)] = 482$ kJ/mol. The associated Gibbs free-energy change at 2000 K is given by $\Delta G_d^0 = -RT \ln K_P = 275$ kJ/mol, showing that the reaction proceeds spontaneously in the direction opposite to that written down above. One should note that all the above values change as the total pressure, P , is altered; the changes can be monitored through experimental observation.

Decomposition of Calcium Carbonate

As another excellent illustrative example, consider the decomposition of calcium carbonate,



for which we set up an equilibrium constant

$$K = f(\text{CO}_2, \text{g})a(\text{CaO}, \text{s})/a(\text{CaCO}_3, \text{s}). \quad (3.4.17)$$

$$\ln(f/P) = \int_0^P (b/RT) dP = bP/RT; \quad f/P = \exp(bP/RT), \quad (3.4.18a)$$

To determine the fugacity of CO_2 , we introduce the following empirical equation: $P\tilde{V} = RT + bP, 42.7 \text{ cm}^3/\text{mol}$, with which, via Eq. (3.1.10) one can determine

$$f = Pe^{0.52P/T} (P \text{ in bar}). \quad (3.4.18b)$$

We next attend to the ratio

$$\frac{a(\text{CaO}, \text{s})}{a(\text{CaCO}_3, \text{s})} = \exp \left[\frac{[\tilde{V}(\text{CaO}, \text{s}) - \tilde{V}(\text{CaCO}_3, \text{s})](P - 1)}{RT} \right], \quad (3.4.19a)$$

where Eqs. (3.4.12) and (3.4.13) have been invoked, on the assumption that the molar volumes are sensibly constant. Density measurements yield values $\tilde{V}(\text{CaO}, \text{s}) = 16.76 \text{ cm}^3/\text{mol}$ and $\tilde{V}(\text{CaCO}_3, \text{s}) = 34.16 \text{ cm}^3/\text{mol} \equiv y$, so that

$$\frac{a(\text{CaO}, \text{s})}{a(\text{CaCO}_3, \text{s})} = \exp \left[\frac{[y](P - 1)}{T} \right] \\ y = -0.212 \text{ bar}^{-1}. \quad (3.4.19b)$$

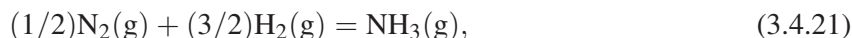
Putting Eqs. (3.4.17), (3.4.18b), and (3.4.19) together, one finally obtains

$$K_P = \left(Pe^{0.52P/T} \right) e^{-0.212(P-1)/T} \\ (P \text{ in bar}). \quad (3.4.20)$$

At 1300 K, the equilibrium pressure is $P = 3.403$ bar; then the second exponential factor in Eq. (3.4.20) has the value 0.9996. This verifies by an illustrative example that the ratio of activities, such as Eq. (3.4.19a), can ordinarily be set equal to unity. The equilibrium constant at 1300 K has the value $K = 3.406$. For any other temperature, the equilibrium constant can be found by inserting the empirical relation for the temperature of interest.

Synthesis of Ammonia from the Elements

The reaction under study is given by



which provides an example of how equilibrium states may be characterized self-consistently. Experimental studies have shown that at 450 °C and at 300 bar, the equilibrium concentration of NH_3 , achieved with an initial 3:1 mixture of $\text{H}_2:\text{N}_2$, stands at 35.82 mol%. Under the prevailing conditions, the gaseous fugacity coefficients are specified by $\gamma(\text{H}_2) = 1.08$, $\gamma(\text{N}_2) = 1.14$, and $\gamma(\text{NH}_3) = 0.91$, as determined by the methodology of Section 3.1. The equilibrium constant for reaction (3.4.21) is specified by

$$K_P = \frac{f(\text{NH}_3)}{f^{1/2}(\text{N}_2)f^{3/2}(\text{H}_2)} = \frac{\gamma(\text{NH}_3)}{\gamma^{1/2}(\text{N}_2)\gamma^{3/2}(\text{H}_2)} \frac{n(\text{NH}_3)}{n^{1/2}(\text{N}_2)n^{3/2}(\text{H}_2)} \frac{n}{P}, \quad (3.4.22)$$

where $n(X)$ is the mole number of species X , n is the total mole number of all species, and P is the total pressure. Initially, $n_0(\text{N}_2)/n = 1/2$, $n_0(\text{H}_2)/n = 3/2$, and $n_0(\text{NH}_3)/n = 0$. Let x be the fraction of NH_3 prevailing at equilibrium, such that $n(\text{N}_2)/n = (1 - x)/2$, $n(\text{H}_2)/n = 3(1 - x)/2$, $n(\text{NH}_3)/n = x$, and $n = 2 - x$. Then at 300 bar,

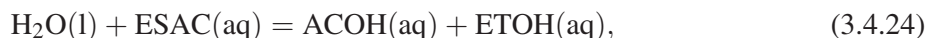
$$K_P = \frac{0.91}{(1.14)^{1/2}(1.08)^{3/2}} \frac{x}{[(1 - x)/2]^{1/2}[3(1 - x)/2]^{3/2}} \frac{2 - x}{300} \text{ bar}^{-1}. \quad (3.4.23)$$

Under prevailing conditions, $x = 0.5275$ whence $K_P = 6.79 \times 10^{-3}/\text{bar}$. Thus, under these conditions, the production of ammonia from its elements is far from complete.

The above also illustrates the arbitrariness in the specification of K_P . The numerical value of the equilibrium constant would have been different if another pressure unit had been used or if some other method of expressing concentrations had been employed. Nevertheless, once the equilibrium constant has been determined for a particular set of physical parameters, this value can be used to determine x for any other set of conditions at the same temperature. The above value of K_P holds so long as P is expressed in bars. It is this feature that renders the concept of equilibrium constants very useful.

Hydrolysis of Ethyl Acetate

As an example of equilibrium in solution, consider the following hydrolysis reaction:



where ESAC \equiv CH₃OCOCH₃, ACOH \equiv CH₃COOH, and ETOH \equiv CH₃CH₂OH stand for acetic acid ester, acetic acid, and ethanol, respectively. The corresponding equilibrium constant has the form given by Eq. (3.4.11),

$$K_m = \frac{a_{\text{ACOH}} a_{\text{ETOH}}}{a_{\text{H}_2\text{O}} a_{\text{ESAC}}} = \frac{m_{\text{ACOH}} m_{\text{ETOH}}}{m_{\text{H}_2\text{O}} m_{\text{ESAC}}} \frac{\Gamma_{\text{ACOH}} \Gamma_{\text{ETOH}}}{\Gamma_{\text{H}_2\text{O}} \Gamma_{\text{ESAC}}}. \quad (3.4.25)$$

Under standard conditions, $m_{\text{H}_2\text{O}} = 55.54$ mol/L, and as a good first approximation, $\Gamma_{\text{H}_2\text{O}} = 1$. For nondissociating chemicals of the type treated here, and in sufficiently dilute solutions, the deviations from ideality may be ignored. One can then determine K_m from a measurement of the observed molality of each component in a very dilute solution. Otherwise the different activity coefficients must be determined as prescribed by Section 3.6. This value of K_m applies to any other solution generated under the same prescribed conditions of temperature and pressure. Once K_m has been fixed in a given experiment, the activities of the three solutes under other conditions are interrelated as shown in Eq. (3.4.25).

3.5 Pressure and Temperature Dependence of Activities and Activity Coefficients

By straightforward combinations of the relationships between activity and chemical potential, we immediately deduce the changes in activities with pressure at constant temperature and composition:

$$(\partial \ln \Gamma_i / \partial P)_{T, x_j} = (\partial \ln a_i / \partial P)_{T, x_j} = [\bar{V}_i(T, P, x_i) - \tilde{V}_i^*(T, 1)] / RT, \quad (3.5.1)$$

where the chemical potentials have been specified relative to standard conditions. Thus, the differentiation $(\partial \mu_i / \partial P)_{T, x_j} = \bar{V}_i$ involved in setting up Eq. (3.5.1) must be executed with care: the partial molal volume of solution is taken at pressure P , so that $\bar{V}_i = \bar{V}_i(T, P)$ for pure i , the standard state is taken at unit pressure, with $\tilde{V}_i^* = \tilde{V}_i^*(T, 1)$.

In like manner, we find at constant pressure and composition

$$(\partial \ln \Gamma_i / \partial T)_{P, x_j} = (\partial \ln a_i / \partial T)_{P, x_j} = -[\bar{H}_i(T, P, x_i) - \tilde{H}_i^*(T, 1)] / RT^2. \quad (3.5.2)$$

Thus, one needs the molar changes in volume and enthalpy when component i is transferred from the pure state at 1 bar to the solution at pressure P and composition x_i .

The changes in Γ_i and a_i with composition must be found empirically as shown next, or specified by use of microscopic theories.

3.6 Determination of Activity Coefficients and Calorimetric Quantities in Chemical Processes

Up to this point, the treatment of activities and activity coefficients has been formal since we have not specified how these quantities may be experimentally determined. We now address this question.

Vapor Pressure Measurements Based on Raoult's Law

One commonly used method involves a measurement of the vapor pressure of a liquid binary solution; at a fixed temperature, the chemical potential of each species in the gas and in the vapor phase is the same. We employ Eqs. (3.3.8) and (3.1.4a) to write

$$\mu_i^{OP}(T) - \mu_i^{*x}(T, 1) = RT \ln[a_i(T, P, x_i)] - RT \ln f_i(T, P, P_i) = RT \ln[a_i(T, P, x_i)/f_i(T, P, P_i)]. \quad (3.6.1)$$

We next introduce the equilibrium condition for pure i in the liquid and vapor phases, for which $x_i = 1$ and $P = P_i^*$, so that

$$\mu_i^{OP}(T) - \mu_i^{*x}(T, 1) = RT \ln[a_i(T, P_i^*, 1)/f_i(T, P_i^*, P_i^*)]. \quad (3.6.2)$$

Equating the above relations leads to

$$a_i(T, P, x_i) = a_i(T, P_i^*, 1) \left[\frac{f_i(T, P, P_i)}{f_i(T, P_i^*, P_i^*)} \right]. \quad (3.6.3)$$

As discussed earlier, the activity of a pure condensed phase is ordinarily close to unity, and the ratio of fugacities may usually be approximated by the ratio of vapor pressures. This leads to the approximate relations

$$a_i(T, P, x_i) \approx P_i/P_i^* \text{ or } \gamma_i(T, P, x_i) \approx P_i/x_i P_i^*, \quad (3.6.4)$$

cited in elementary texts. The physical significance is perhaps best illustrated in Figure 3.6.1. For a solution of composition x_i , the quantity $x_i P_i^*$ is represented by the arrow \overline{AC} , which represents the

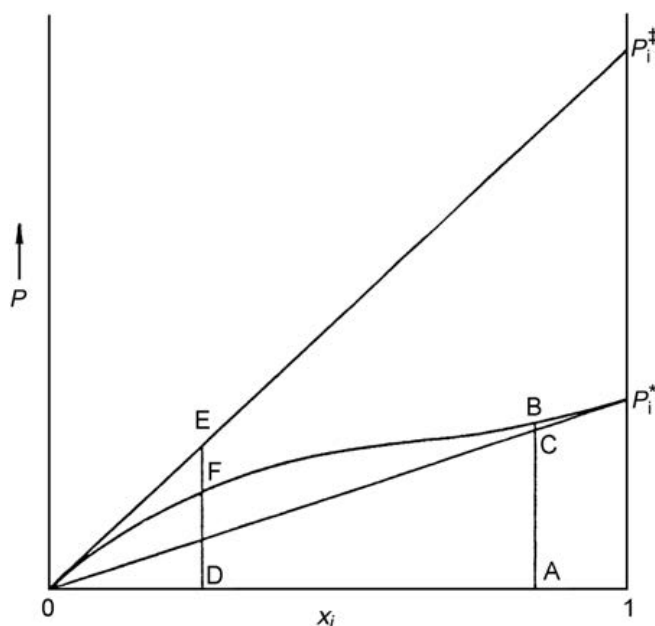


FIGURE 3.6.1

Diagram illustrating the determination of activity coefficients relative to the pure solvent (ACB) with vapor pressure P_i^* , and to infinite dilution (DFE), based on Henry's law, associated with the extrapolated pressure P_i^\ddagger .

vapor pressure that would prevail if the solution were ideal. By contrast, P_i (arrow of length \overline{AB}) represents the vapor pressure of the actual solution, involving Raoult's Law in these calculations. This experimental approach is useful primarily when the species of interest is the solvent. In more accurate calculations, one must determine the fugacities by the methods of Eq. (3.4.12) and (3.4.13) and the activities of the pure phases by the methods of Section 3.4.

Equations (3.6.3) and (3.6.4) are in a sense deceptive; for, they can only be used for use in the determination of P_i^* if component i exists as a pure liquid at the temperature of the measurement. Often this is not the case, such as the dissolution of common gases or of sugar in water at room temperature. This forces us to consider an alternative that is discussed next.

Vapor Pressure Measurements Based on Henry's Law

The alternative procedure rests on the choice of a reference solution at infinite dilution. This method is useful if the component under study is the solute, or if the solution component of interest does not exist in a pure condensed state under the conditions of the experiment. At very great dilution, the vapor pressure of the solute obeys *Henry's Law*, $P_i = K_{Hx_i}$, in the limit $x_i \rightarrow 0$. That is, a plot of P_i vs x_i is linear in this range, as is depicted in Figure 3.6.1. The straight line shows the vapor pressure of i if this component were to obey Henry's Law over the entire composition range. Based on this scheme, one selects as a standard the *hypothetical Henry's Law substance i in pure form*, that is produced by extrapolating Henry's Law to $x_i = 1$, where its vapor pressure would be. The fact that actual solutions do not remotely behave in this manner need be no deterrent to the use of as a reference state. This choice, rather than being an absurd procedure, is a matter of convenience. For near-infinite dilution, the solute molecules are nearly isolated and their interactions become negligibly small. The fictitious Henry's Law material thus has properties akin to an assembly of ideal, noninteracting units that has always served as a good reference standard. The reason for this choice will be further clarified in our subsequent development.

For the present choice of standard, Eq. (3.6.1) remains applicable as before. However, the gas phase of the hypothetical material would have a chemical potential of the form $\mu_i = \mu_i^{OP}(T) + RT \ln f_i(T, P_i^\ddagger, P_i^\ddagger)$ and in the condensed state, the form (3.1.4), with P replaced by P_i^\ddagger . Hence, in place of Eq. (3.6.2), we now have

$$\begin{aligned} \mu_i^{OP}(T) - \mu_i^{*x}(T, 1) &= RT \ln \left[a_i^{*x}(T, P_i^\ddagger) \right] - RT \ln f_i(T, P_i^\ddagger, P_i^\ddagger) \\ &= RT \ln \left[a_i(T, P_i^*, 1) / f_i(T, P_i^\ddagger, P_i^\ddagger) \right]. \end{aligned} \quad (3.6.5)$$

When account is taken of Eq. (3.6.1), one obtains

$$a_i(T, P, x_i) = a_i(T, P_i^*, 1) \left[\frac{f_i(T, P, P_i)}{f_i(T, P_i^\ddagger, P_i^\ddagger)} \right], \quad (3.6.6)$$

To a good degree of approximation, this relations reduces to

$$a_i(T, P, x_i) \approx P_i / P_i^\ddagger \quad \text{or} \quad \gamma_i(T, P, x_i) \approx P_i / x_i P_i^\ddagger. \quad (3.6.7)$$

To use this result, one must execute detailed measurements of the vapor pressures of the actual solutions at great dilution, where Henry's Law is obeyed. Extrapolation of the resulting straight line to the composition of pure solvent then establishes. In this case the vectors \overline{DE} and \overline{DF} in Figure 3.6.1 correspond to a_i and P_i respectively. A measurement of P_i at the particular composition x_i then yields the activity or activity coefficient in this regime. For more precise work, Eq. (3.6.6) must be used in the manner discussed earlier.

One must not adhere to the mistaken notion that the analysis leading to Eqs. (3.6.3) and (3.6.4) should be used in the upper range of x_i and that the analysis leading to Eqs. (3.6.6) and (3.6.7) should be used in the lower range. The two approaches are based on the use of different reference states, P_i^* , and P_i^\ddagger , and are therefore not interchangeable; one must stay with one or the other scheme.

Applications of Henry's Law

The utility of Henry's law is illustrated by the following discussion:

For volatile components, one invokes the equilibrium at fixed temperature T between the substance in the vapor phase and in the dissolved state, at activities a_v and a_l , respectively. This equilibrium state is characterized by the relation

$$K_H = a_v/a_l \approx P_v/a_l \approx P_v/x_l, \quad (3.6.8)$$

that invites comparison with Eq. (3.6.7). The right-hand side is applicable to dilute solutions and low vapor pressures, and thereby may be used to determine $K_H \equiv P_i^\ddagger$, which is seen to be Henry's Law constant in disguise. Once this quantity is known, Eq. (3.6.8) is used to find a_l for any other concentration at which P_v or a_v can be measured. The extension of this elementary argument to the more refined relation (3.6.6) is straightforward.

The use of Henry's law for nonvolatile materials is indirect. We use the Gibbs–Duhem relation $x_1 d\mu_1 + x_2 d\mu_2 = x_1 d \ln a_1 + x_2 d \ln a_2 = 0$ in the range where Raoult's law applies to component 1, which is the solvent; whence $a_1 = x_1$, $x_1 d \ln a_1 = dx_1$, and

$$d \ln a_2 = -dx_1/x_2 = dx_2/x_2 = d \ln x_2; \quad d \ln(a_2/x_2) = 0. \quad (3.6.9)$$

On integrating, we find that $a_2/x_2 = K_R$, where the constant is fixed at a given temperature. Now use Henry's law in the form $a_2 = P_2/P_2^\ddagger$, whence $P_2 = K_R P_2^\ddagger x_2$, which shows that $K_R = 1$, and that *under conditions where Raoult's law applies to the solvent, Henry's law holds for the solute*. This simple relationship obviously applies only to very dilute solutions. The activity of the nonvolatile component can thus be determined by measuring the vapor pressure of the solvent in its dependence on the composition of the solution and then introducing the Gibbs–Duhem relation.

Conventionally, measurements based on the above scheme are couched in terms of the molality m . Here the Henry's law constant is found by plotting P vs m for dilute solutions and then determining the extrapolated vapor pressure value P° that corresponds to unit molality. For aqueous solutions and small m ,

$$x_1 = 1 - x_2 = 1 - \frac{n_2}{n_1 + n_2} = 1 - \frac{m}{1000/M_1 + m} \approx 1 - \frac{m}{55.506}. \quad (3.6.10)$$

In the range where Raoult's law applies $a_1 = x_1$, so that

$$\ln a_1 = \ln x_1 = \ln(1 - m/55.506) \approx -m/55.506. \quad (3.6.11a)$$

For further progress, one introduces the so-called *osmotic coefficient* ϕ through the relation, modeled after Eq. (3.6.11a),

$$\ln a_1 = -m\phi/55.506, \quad (3.6.11b)$$

where $\phi = 1$ in sufficiently dilute solutions. Then, measurements of the vapor pressure of water over the solution yields $a_1 = P_1/\widehat{P}$, from which ϕ may be determined. Now the Gibbs–Duhem relation is invoked in the form

$$55.506 \, d \ln a_1 + m \, d \ln a_2 = 0. \quad (3.6.12)$$

Define the activity coefficient referred to molality of the solute by γ_2 . Use of Eq. (3.6.11b) in Eq. (3.6.12) leads to $m \, d \ln(m\gamma_2) = d(\phi m)$, or

$$d \ln \gamma_2 = d\phi + ((\phi - 1)/m)dm, \quad (3.6.13a)$$

which is then integrated between the limits 0 to m , with $\gamma_2 = 1$ and $\phi = 1$ at $m = 0$. This leads to the final relation of interest,

$$\ln \gamma_2 = \phi - 1 + \int_0^m [(\phi - 1)/m]dm. \quad (3.6.14)$$

Thus, a plot of $(\phi - 1)/m$ vs m yields the value of the integral, whence the activity coefficient of interest may be determined experimentally.

The accurate vapor pressure measurements required in such experiments are difficult to execute. Therefore, an indirect experiment is generally adopted. One carries out precise measurements, and applies Eqs. (3.6.11) and $\alpha_1 = P_1/\widehat{P}$ to a particular reference system, such as sucrose dissolved in water, to determine the value of ϕ_r that corresponds to a particular molality m_r in this reference solution. One then prepares an aqueous solution of the unknown at roughly comparable molality m , and allows the two solutions to equilibrate in an isolated environment containing only water vapor in the gas phase. At equilibrium, the water activity is the same over both solutions, so that by Eq. (3.6.11b), the following equality holds:

$$m_r \phi_r = m \phi. \quad (3.6.15)$$

A measurement of m then permits ϕ to be established. The process is repeated for many different m_r and m values, so that the corresponding activity of the dissolved unknown species may be found via Eq. (3.6.14). This procedure is known as the *isopiestic method*.

In the next chapter, we show that Henry's law is also essential to the specification of the activities of electrolytes.

Calorimetric Functions of State in Chemical Processes

Up to now, we have considered of chemical processes that have been brought to equilibrium. We have learned how to determine activities and the use of Raoult's Law and Henry's Law. We now focus on a rather different but related subject, the characterization of actual chemical processes. This requires construction of methods for calculating the enthalpy, entropy, and free-energy changes for any given chemical reaction²; this involves some of the above procedures.

Standard Enthalpies of Elements

We begin with the individual thermal properties of all elements and compounds involved in a given reaction. Since one cannot assign a unique value to the energetics of any material, we need to set up conventions that govern the energy changes. Rather than introducing generalities that are hard to digest, we introduce specific examples to illustrate the general point.

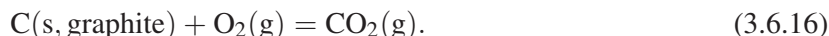
We begin with the characterization of pure elements: by convention,

at any temperature T of interest the enthalpy of a pure element in its most stable state at that T and at a pressure P of 1 bar shall be assigned the value zero.

With 1 bar as the *standard state*, the standard molar enthalpy of pure i at temperature T is represented by the symbol $\tilde{H}_{i,T}^{\circ} = 0$; the asterisk is ordinarily omitted, it being understood that element i is in its pure state. One must be careful in the application of this rule: for example, the stable configuration of carbon at room temperature and ambient pressure is graphite rather than diamond. In the same vein, sulfur under these conditions is stable in the rhombic habit, which is its proper reference state. Under these conditions, the reference state for Sn is the white, rather than the gray crystalline habit. As another example, Br_2 at $P = 1$ bar and 300 K is a liquid; however, if used in reactions at 500 K, the reference configuration for Br_2 is its gaseous state.

Standard Enthalpies of Formation of Compounds

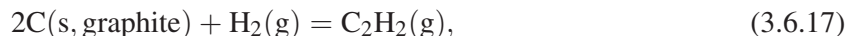
Standard enthalpies of formation of compounds are determined by adopting the chemical reaction that produces the material of interest from its constituent elements. As an example, consider the formation of carbon dioxide,



When the reaction is executed at a total pressure of 1 bar at $T = 298.15$ K (try to design a hypothetical set of conditions such that the total pressure during the reaction remains at 1 bar; see Exercise 3.6.3), calorimetric measurements yield a value of -393.5 kJ per molar advancement of the reaction. Since by convention, $\tilde{H}_{i,T}^{\circ} = 0$ for graphite and for O_2 gas at 1 bar, the above enthalpy is taken as the standard (molar) enthalpy of formation; i.e., $\Delta\tilde{H}_{f,298.15}^{\circ} = -393.15$ kJ, for 1 mol of $\text{CO}_2(\text{g})$ at a pressure of 1 bar at 298.15 K.⁴ More generally,

The standard (molar) heat of formation $\Delta\tilde{H}_{f,T}^{\circ}$ of a compound is the measured enthalpy change in the formation of 1 mol of the compound at a pressure of 1 bar and at temperature T from its constituent elements in their most stable state.

In the above example, the CO_2 formation was exothermic; the enthalpy of the compound is more stable than that of the elements from which it is formed. A contrary example is furnished through the reaction



for which $\Delta\tilde{H}_{f,298.15}^{\circ} = +226.7$ kJ/mol at room temperature, showing that C_2H_2 is energetically less stable than hydrogen gas and graphite.

The actual determination of heats of formation of compounds often requires a rather involved set of steps, which is generically represented as follows: (1) For gaseous elements, one calculates for each gas the ΔH needed to change from the ideal gas state at temperature T and at 1 bar to the real gas under

the same conditions, using the procedures cited in Sections 1.12. and 3.1.⁵ (2) The enthalpy of mixing of the pure elements at T and 1 bar are determined as specified by Section 3.8. If deviations from ideality are important, the procedure of Sections 3.1–3.5 must be utilized. (3) The enthalpy change must be computed for altering each of the reagents from T and 1 bar to the conditions of the reaction, T_R and P_R . For this purpose, one generally employs a relation of the form

$$\Delta H = \int_T^{T_R} C_P dT + \int_P^{P_R} (V - TV\alpha) dP, \quad (3.6.18a)$$

where the second term derives from Eq. (1.12.10b). (4) The reaction is carried out, starting with the reagents under the conditions specified in Eq. (3.6.18a); the resulting enthalpy of formation of the compound is determined calorimetrically. (5) The enthalpy change is computed via Eq. (3.6.18a) for bringing the product from the final equilibrium configuration at T_R and P_R back to temperature T and 1 bar. (6) For a gaseous product, one determines the enthalpy change in bringing gases from their actual state to their ideal state at T and 1 bar. (7) To list the enthalpy of formation at some temperature other than T , one may use the relation

$$\Delta \tilde{H}_{T',f}^0 - \Delta \tilde{H}_{T,f}^0 = \int_T^{T'} \tilde{C}_P(T) dT. \quad (3.6.18b)$$

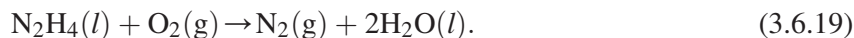
The overall enthalpy change determined in all the above steps is clearly very different from the equilibrium quantity ΔH_d introduced in Section 2.9.

Standard Enthalpies of Reaction

Using the above procedure, an extensive tabulation of $\Delta \tilde{H}_{f,T,i}^0$ values has been built up for a large collection of compounds. Once that is available, the *standard enthalpy change* for any chemical reaction² $\sum_i \nu_i A_i \rightarrow 0$ of interest may be established from the general relation,

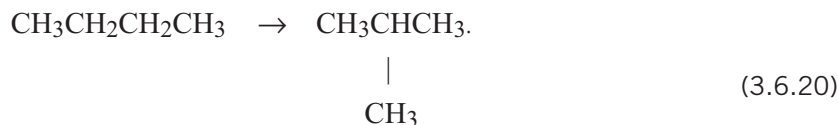
$$\Delta \tilde{H}_{RX}^0(T) = \sum_i \nu_i \Delta \tilde{H}_{f,i}^0(T). \quad (3.6.18c)$$

As an example, consider the reaction

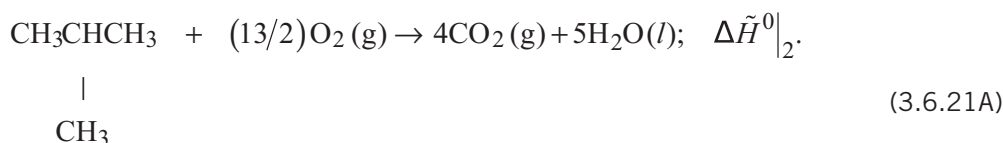


Set at zero the standard enthalpies of the elements; then employ the quantities $\Delta \tilde{H}_{f,i}^0 = 50.42$ kJ/mol and -285.84 kJ/mol for hydrazine and water, respectively at 298 K and 1 bar. On adding up these values algebraically (with due regard to the fact that the ν_i for reagents are negative), one finds that $\Delta \tilde{H}_{RX}^0 = -622.09$ kJ/mol. Here the “/mol” designation indicates that the calculation applies to 1 mol of advancement of the reaction as written (i.e., with $\lambda = 1$ mol). It thus involves 1 mol of hydrazine or oxygen as reagents, and 1 mol of formation of nitrogen, while the enthalpy change per mole of water is half of the above. Again, these enthalpy changes must be clearly distinguished from the quantity ΔH_d .

A very interesting example has been provided by P. A. Rock.⁶ It deals with the isomerization reaction of *n*-butane to isobutane



Reaction (3.6.20) is always accompanied by several competing reactions, so that it is difficult to determine the standard enthalpy of isomerization by direct experimental measurements. To circumvent this problem, one can determine the combustion of both isomers under standard conditions:



One then adds the measured enthalpies algebraically to obtain $\Delta\tilde{H}_{RX}^0 = \Delta\tilde{H}^0|_1 - \Delta\tilde{H}^0|_2 = -6.862 \text{ kJ/mol}$, showing that the isomer is the slightly more stable configuration.

Temperature Variation of Standard Enthalpy Changes

Generally, standard enthalpy changes are tabulated at $T = 298.15 \text{ K}$. To convert these values to any other temperature, we use the basic relation $d\tilde{H}_i|_p = \tilde{C}_{iP}dT$, to write, as in Eq. (3.6.18c), $d(\Delta\tilde{H}^0) = d(\Delta\tilde{C}_P^0)dT$, with $\Delta\tilde{C}_P^0 \equiv \sum_i \nu_i \tilde{C}_{iP}^0$, so that

$$\Delta\tilde{H}^0(T_2) - \Delta\tilde{H}^0(T_1) = \int_{T_1}^{T_2} \Delta\tilde{C}_P^0(T)dT. \quad (3.6.22)$$

The temperature variation of the heat capacity of each participant in the chemical reaction must be specified so that the integration can be carried out. One must be careful not to extend the temperature interval of integration over such wide limits that changes in phase or in the most stable form of the elements or compounds are encountered.

Applications

It hardly requires much commentary to note that thermochemical information is largely used to categorize the usefulness of chemical reactions as sources of energy. Much of the energy needs of the world are met through combustion of petrochemicals or coal. The enthalpy values then provide listings to show what types of combustion processes yield the optimal energy outputs. For example, tabulations indicated a large enthalpy output when dimethyl hydrazine is combined with dinitrogen tetroxide. The reaction is spontaneous, a feature that led to its use in the Apollo Lunar Lander missions. Ammonium perchlorate is another energy source of considerable use: its decomposition gives rise to many gaseous products that together with the energy released, is used as a thruster in rockets.

Entropy Changes in Chemical Reactions

Entropy changes accompanying a particular chemical reaction $\sum_i \nu_i A_i \rightarrow 0$ are handled by writing

$$\Delta \tilde{S}_{T_{RX}}^0 = \sum_i \nu_i \tilde{S}_{i,T}^0. \quad (3.6.23)$$

The individual molar entropies under standard conditions of the various participating species are generally available in tabular form; these are constructed as shown in Section 1.15. Alternatively, they are found via an empirical equation of state, using Maxwell relations, as in entries [7], [8] of Table 1.12. II, followed by integration; the temperature of the reaction is a parameter. As explained in Section 1.13, if nuclear effects are excluded, or any frozen-in disorder remains undisturbed, (or any nonequilibrated condition is not altered), one may set the *entropy of all participants in the reaction, whether they be elements or compounds, equal to zero at $T = 0$* . This then establishes an absolute scale for the tabulated entropies of the reagents and products at any temperature T . You should try to set up strategies for determining $\Delta \tilde{S}_{T_{RX}}$ for reactions under other than standard conditions; see Exercise 3.6.8.

As an example, examine the reaction



for which $\tilde{S}_{298.15}^0 (\text{J/K} - \text{mol}) = 41.63, 205.03, 43.64$, respectively; moreover, $\tilde{C}_{P,298.15}^0 (\text{J/K} - \text{mol}) = 25.40, 29.35, 40.25$ for Zn, O₂, and ZnO, respectively. Thus, for the reaction as written, $\Delta \tilde{S}_{298.15}^0 = -41.63 - 102.52 + 43.64 = -100.51 \text{ J/K} - \text{mol}$. Also, on ignoring any change of heat capacity with temperature, we calculate the entropy change at 100 °C as, $\Delta \tilde{S}_{398.15}^0 = \Delta \tilde{S}_{298.15}^0 + \Delta \tilde{C}_{298.15}^0 \ln(398.15/298.15) = -100.51 + (40.25 - 14.67 - 25.40) \ln 1.134 = -100.56 \text{ J/K} - \text{mol}$, a very small change in the entropy over a 100° C interval.

Standard Gibbs Free-Energy Changes

The standard Gibbs free-energy changes accompanying a chemical reaction are handled in a manner completely analogous to that described in the preceding subsections. By convention,

at any temperature T of interest the Gibbs free energy of a pure element in its most stable state at that T and at a pressure P of 1 bar shall be assigned the value zero.

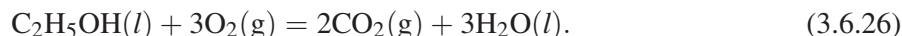
Sometimes the requirement of the most stable configuration is dropped, but this cannot be done if one also involves calculations of enthalpy changes.

The standard Gibbs free energies of formation of compounds are based on appropriate synthetic reactions in a manner analogous to the determination of enthalpies of compounds from their elements. For more general reactions, one writes

$$\Delta \tilde{G}_f^0(T) = \sum_i \nu_i \Delta \tilde{G}_{f,i}^0(T). \quad (3.6.25)$$

where the Gibbs free energies of formation of the compounds, $\Delta \tilde{G}_{f,T,i}^0$, are available from tabulations, usually compiled at 300 K; the entries are generally based on calculations via $\Delta \tilde{G}_{f,T,i}^0 = \Delta \tilde{H}_{f,T,i}^0 - T \Delta \tilde{S}_{f,T,i}^0$. Other methods include emf determinations, taken up in the next chapter.

As an example, consider the reaction at 298.15 K:



One may consult tabulations of molar Gibbs free energies to find $\Delta\tilde{G}_{298.15}^0(\text{kJ/mol}) = -174.89, 0, -394.36, -237.18$ for the species written out left to right in Eq. (3.6.26). Accordingly, $\Delta\tilde{G}_{298.15}^0 \text{RX} = 3(-237.18) + 2(-394.36) - (-174.89) = -1325.37 \text{ kJ/mol}$ at 298.15 K. The free-energy change at 50 °C is found by consulting the entropy listings for the species in the order of Eq. (3.6.26), left to right: $\tilde{S}_{298.15}^0(\text{J/mol}) = 160.7, 205.03, 213.64, 69.91$. Neglecting the changes of entropy with temperature over the indicated interval, we then note that $\Delta\tilde{G}_{348.15}^0 \text{RX} = -1325.37 - (50)[3(69.91) + 2(213.64) - 3(205.03) - 160.7] = -1318.41 \text{ kJ/mol}$, a small change relative to the room temperature value.

Tabulations

With assignment of zero for the standard enthalpies of pure elements, one may equate $\Delta\tilde{H}_{f,i,T}^0$ with the standard enthalpy of the compound species i , $\tilde{H}_{i,T}^0$. This quantity at temperature T may then be taken relative to the molar enthalpy at 298 K or at 0 K, namely $\tilde{H}_{i,298}^0$ or $\tilde{H}_{i,0}^0$. The difference is ordinarily tabulated as $(\tilde{H}_{i,T}^0 - \tilde{H}_{i,298}^0)/T$, or as $(\tilde{H}_{i,T}^0 - \tilde{H}_{i,0}^0)/T$, since these ratios vary only slowly with temperature. Of course one also encounters tabulations of $(\tilde{H}_{i,298}^0 - \tilde{H}_{i,0}^0)/T$, but they tend to be less complete.

One may then adjoin the standard molar entropies to obtain

$$(\tilde{G}_{i,T}^0 - \tilde{H}_{i,298}^0)/T = (\tilde{H}_{i,T}^0 - \tilde{H}_{i,298}^0)/T - \tilde{S}_{i,T}^0 \quad (3.6.27a)$$

and

$$(\tilde{G}_{i,T}^0 - \tilde{H}_{i,0}^0)/T = (\tilde{H}_{i,T}^0 - \tilde{H}_{i,0}^0)/T - \tilde{S}_{i,T}^0. \quad (3.6.27b)$$

For interpolation purposes one may use the relationship, valid at $P = 1$ bar:

$$\tilde{G}_i^0(T_2) - \tilde{G}_i^0(T_1) = \int_{T_1}^{T_2} \tilde{S}_i^0(T) dT. \quad (3.6.28)$$

We call attention one last time to the difference between the change in Gibbs free energy invoked here and the differential Gibbs free energy expression that was set up in Section 2.9, while discussing chemical equilibrium.

Integral vs Differential Heats of Dilution

Heats of solution are not constant but generally vary with concentration of the components. For example, when HCl is dissolved in water, $\Delta H/m$ changes from -17.9 to -17.4 kcal/mol as one proceeds from unit molality to infinite dilution. To handle such cases, one distinguishes between *integral heats of solution*, $\Delta H/m$, and *differential heats of solution*, $(\partial\Delta H/\partial m)_{T,P}$ that pertain to the addition of an infinitesimal amount of solvent to a solution of molality m .

The two heats may be related in the following manner: Let $H, \tilde{H}_1^*, \tilde{H}_2^*$ represent the enthalpy of a binary solution and of components 1 and 2 in pure form relative to any arbitrary standard value for the enthalpy. Then the enthalpy of mixing of n_1 moles of solvent and n_2 moles of solute is given by

$$\Delta H = H - n_1 \tilde{H}_1^* - n_2 \tilde{H}_2^*, \quad (3.6.29)$$

so that the differential heat of solution with respect to mole numbers reads

$$(\partial \Delta H / \partial n_2)_{T,P,n_1} = (\partial H / \partial n_2)_{T,P,n_1} - \tilde{H}_2^* \equiv \bar{H}_2 - \tilde{H}_2^* \equiv (\bar{H}_2 - \bar{H}_2^0) - (\tilde{H}_2^* - \bar{H}_2^0) \equiv \bar{L}_2 - \tilde{L}_2^*, \quad (3.6.30)$$

where the enthalpies were determined relative to those at infinite dilution, \tilde{H}_2^0 .

For the solvent, one finds by analogy:

$$\partial \Delta H / \partial n_1 = \bar{H}_1 - \tilde{H}_1^*. \quad (3.6.31)$$

Adiabatic Combustion of Methane

As an illustration of the above exposition, we consider the adiabatic combustion of methane and ask for the final temperature that may be achieved in this process. The relevant reaction is written as



Initially $\text{CH}_4(\text{g})$ is heated in an inert atmosphere to 573 K. Air is then admitted and the reaction is allowed to go to completion. For later use, one requires molar heat capacity tabulations for all the species in the above reaction.

Since a direct determination of the final temperature is difficult, we consider a sequence of steps for which the enthalpy changes may be readily determined, and which are then summed. (i) Cool the products from the final temperature T_f to 298.15 K. (ii) Cool the reagents from the starting temperature of 573.15–298.15 K. (iii) Carry out the reaction at 298.15 K; here the tabulated heats of formation may be used in conjunction with Eq. (3.6.18c) to determine the corresponding enthalpy change, given by $\Delta \tilde{H} = \Delta \tilde{H}_i + \Delta \tilde{H}_{ii} + \Delta \tilde{H}_{iii} = 0$ for an adiabatic process. This may be translated into the following equation:

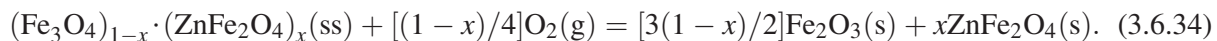
$$\begin{aligned} & n[\text{CO}_2(\text{g})] \int_{298}^{T_f} \tilde{C}_p[\text{CO}_2(\text{g})] dT + n[\text{N}_2(\text{g})] \int_{298}^{T_f} \tilde{C}_p[\text{N}_2(\text{g})] dT \\ &= -\Delta \tilde{H}_{298}^0 - n[\text{CH}_4(\text{g})] \int_{473}^{298} \tilde{C}_p[\text{CH}_4(\text{g})] dT - n[\text{O}_2(\text{g})] \int_{473}^{298} \tilde{C}_p[\text{O}_2(\text{g})] dT \\ &\quad - n[\text{N}_2(\text{g})] \int_{473}^{298} \tilde{C}_p[\text{N}_2(\text{g})] dT. \end{aligned} \quad (3.6.33)$$

Here one must note that all the oxygen was used up in the combustion process, whereas $n[\text{N}_2(\text{g})] = 2(0.79/0.21)$ is the number of moles of N_2 present in the air that was used in the combustion process. On inserting the relevant relations for the various molar heat capacities and inserting the known value for the molar enthalpy of step (iii), one may numerically determine the upper limit, T_f , of the integrals on the left of Eq. (3.6.33). This yields a value of $T_f = 2265$ K, which is an upper limit, since the reaction is not totally adiabatic, is not 100% complete, and because some dissociation of the products takes place at the elevated temperatures achieved in the combustion.

Oxidation Boundary for Magnetite–Zinc Ferrite Solid Solutions

Here we cite a somewhat esoteric example to show how the standard chemical potentials—which so far have been left unspecified—can actually be determined experimentally. Consider the properties of a Fe_3O_4 – ZnFe_2O_4 – Fe_3O_4 solid solution at the oxidation boundary separating hematite (Fe_2O_3) from magnetite-based zinc ferrite $\text{ZnFe}_2\text{O}_4|\text{Fe}_3\text{O}_4$ solid solutions.¹ To characterize the oxidation, we proceed with the following steps.

First, write down the chemical reaction that schematizes the oxidation process, namely,



The solid solution (ss) on the left has been represented as a mixture consisting of $1-x$ moles of magnetite and x moles of zinc ferrite per formula unit of ss. It is assumed that the zinc ferrite moiety remains passive while any changes relating to the oxygen/cation composition occur exclusively in the magnetite component.

The free-energy change accompanying reaction (3.6.34) at constant T and P is specified by

$$\begin{aligned} \Delta G(1) = & -\mu[(\text{Fe}_3\text{O}_4)_{1-x} \cdot (\text{ZnFe}_2\text{O}_4)_x(\text{s})] - [(1-x)/4]\mu[\text{O}_2(\text{g})] \\ & + [3(1-x)/2]\mu[\text{Fe}_2\text{O}_3(\text{s})] + x\mu[\text{ZnFe}_2\text{O}_4(\text{s})]. \end{aligned} \quad (3.6.35)$$

For solids, we adopt Eq. (3.3.6), to read $\mu_i(T, 1) = \mu_i^*(T, P) + RT \ln a_i(T, P, x)$, and for gases, we set $\mu_g(T, P) = \mu_g^{OP}(T) + RT \ln P$, thereby ignoring deviations from ideality in the gas phase. For simplicity, we further assume that we may set

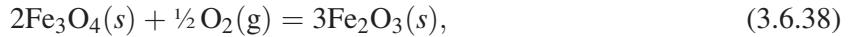
$$\mu[(\text{Fe}_3\text{O}_4)_{1-x} \cdot (\text{ZnFe}_2\text{O}_4)_x(\text{s})] = x\mu[\text{ZnFe}_2\text{O}_4(\text{s})] + (1-x)\mu[\text{Fe}_3\text{O}_4(\text{sss})], \quad (3.6.36)$$

where $\mu[\text{Fe}_3\text{O}_4(\text{sss})]$ stands for the chemical potential of the Fe_3O_4 component that forms the spinel solid solution (sss) with ZnFe_2O_4 , which must be carefully distinguished from $\mu^*[\text{Fe}_3\text{O}_4(\text{s})]$, that represents the chemical potential of pure magnetite. On applying Eq. (3.6.36) to Eq. (3.6.35), we find

$$\begin{aligned} \Delta G(1) = & -1(1-x)\mu[\text{Fe}_3\text{O}_4(\text{sss})] - [(1-x)/4]\mu[\text{O}_2(\text{g})] + [3(1-x)/2]\mu[\text{Fe}_2\text{O}_3] \\ = & -(1-x)\mu^*[\text{Fe}_3\text{O}_4(\text{s})] - [(1-x)/4]\mu^{OP}[\text{O}_2(\text{g})] + [3(1-x)/2]\mu^*[\text{Fe}_2\text{O}_3(\text{s})] \\ & - (1-x)RT \ln a[\text{Fe}_3\text{O}_4(\text{sss})] - [(1-x)/4]RT \ln P[\text{O}_2(\text{g})]. \end{aligned} \quad (3.6.37)$$

At equilibrium, $\Delta G(1) = 0$. Here $P[\text{O}_2(\text{g})]$ stands for the oxygen pressure prevailing during the oxidation.

Next, consider the following oxidation step that converts magnetite to hematite, carried out under the conditions prevailing at the oxidation boundary:



for which the corresponding free-energy change is

$$\Delta G(S) = -2\mu^*[\text{Fe}_3\text{O}_4(s)] - \frac{1}{2}\mu^{OP}[\text{O}_2(g)] - \frac{1}{2}RT \ln P[\text{O}_2(\text{M} - \text{H})] + 3\mu^*[\text{Fe}_2\text{O}_3(s)] = 0, \quad (3.6.39)$$

where $P[\text{O}_2(\text{M} - \text{H})]$ is the oxygen pressure prevailing at the magnetite–hematite boundary. In the literature, the following empirical formula has been proposed: $\log P[\text{O}_2(\text{M} - \text{H})] = -24,634/T + 13.96$ bar. When this expression is inserted in Eq. (3.6.39), one finds

$$-\mu^*[\text{Fe}_3\text{O}_4(s)] - (1/4)\mu^{OP}[\text{O}_2(g)] + (3/2)\mu^*[\text{Fe}_2\text{O}_3(s)] = 2.303RT[-24,634/T + 13.96]/4. \quad (3.6.40)$$

This solves the task at hand, namely, we have shown how the appropriate combination of chemical potentials under standard conditions has been determined empirically at any temperature T .

As the third step, we can specify the equilibrium vapor pressure at the two-phase boundary: insert Eq. (3.6.40) into Eq. (3.6.37), so as to solve for

$$\log P[\text{O}_2(\text{M} - \text{H})] = -4 \ln a[\text{Fe}_3\text{O}_4(sss)] + 2.303RT[-24,634/T + 13.96]/4. \quad (3.6.41)$$

In first approximation $a = 1$, so that the first term on the right drops out. To improve on this step, one may use Eq. (3.4.12) to determine the logarithmic contribution, but in view of the approximations introduced earlier, it is doubtful whether such a step is justified. Leaving this step aside, a typical value at $T = 1500$ K leads to $P(\text{O}_2) = 3.45 \times 10^{-3}$ bar.

The Acetylene–Benzene Conversion

Consider the possibility of converting acetylene gas ($\text{C}_2\text{H}_2, \text{Ac}$) to liquid benzene ($\text{C}_6\text{H}_6, \text{Bz}$) according to $3\text{C}_2\text{H}_2(g) = \text{C}_6\text{H}_6(l)$. At 298.15 K, the molar free energies of formation are specified as 124.5 and 209.2 kJ, respectively. Then,

$$\Delta G_{298.15}^0 = 124.5 - 3(209.2) = -503.1 \text{ kJ} = -RT \ln K_{eq} = -RT \ln \frac{a_{\text{Bz}(l)}}{a_{\text{Ac}(g)}^3}. \quad (3.6.42)$$

At reasonably low pressures, we may set $a_{\text{Bz}(l)} = 1$ bar and $a_{\text{Ac}(g)} = P_{\text{Ac}(g)}$. On taking $R = 8.3124 \text{ J K}^{-1} \text{ mol}^{-1}$, we can solve for

$$P = \exp(-503.1 \times 10^3 / 3 \times 8.314 \times 298.15) = 4.1 \times 10^{-30} \text{ bar}, \quad (3.6.43)$$

a tiny number, showing that under normal storage conditions, acetylene should convert to benzene, as is also clear by determining the value of the equilibrium constant, $K = 203$. That Ac can nevertheless be safely stored without detectable Bz formation indicates that the reaction is kinetically hindered. If a suitable catalyst can be found, the above reaction would provide a suitable method for the production of benzene.

References and Commentary

- 3.6.1.** P. Wang, Q.W. Choi, J.M. Honig, *Z. anorg. allg. Chem.* **550**, 91 (1987).
- 3.6.2.** Up to this point, we have designated the chemical reaction as $\sum_i \nu_i A_i = 0$. This was to indicate that we treated the process as having come to a quiescent state, only small deviations from equilibrium being permitted. In this section, we consider actual chemical reactions that are permitted to proceed on a macroscopic scale; the corresponding reaction will be designated as $\sum_i \nu_i A_i = 0$.
- 3.6.3.** Devise a hypothetical set of conditions under which reaction (3.6.16) can be carried out at a pressure of 1 bar.
- 3.6.4.** Sometimes, for convenience, the designation $T = 298.15$ K is abbreviated to read 298 K; occasionally one even encounters the designation 300 K, which is taken to be room temperature.
- 3.6.5.** This step is necessary because, by convention, the standard state of a real gas is actually the hypothetical state of the ideal gas at 1 bar. Allowance must be made for the difference between these two states in exact determinations. Since the enthalpy of an ideal gas is independent of pressure, the difference between its value and that of the real gas may be determined by integrating Eq. (1.12.10b) between pressure 1 and pressure P . In general, this value tends to be very small compared to the contribution from all other steps.
- 3.6.6.** P. A. Rock, *Chemical Thermodynamics* (University Science Books, Mill Valley, CA, 1983), p. 195 ff.
- 3.6.7.** Describe procedures that can be used to change from standard enthalpy changes to standard energy changes.
- 3.6.8.** To determine entropies of reactions under conditions different from 298.15 K and 1 bar, revert to appropriate expression for the variation of the individual entropies, S_i , with T and P . Identify two methods that can be used for this purpose. Set up the requisite expressions and discuss your strategies.
- 3.6.9.** Devise strategies for determining enthalpy changes and Gibbs free-energy changes at pressures different from 1 bar.

3.7 Determination of Activities from Freezing Point Lowering of Solutions

Activity of the Solvent

Having dealt earlier with the solute, we now study the determination of the activity of the solvent. This is achieved by direct analogy to Eq. (2.8.8), which applies to solutions in equilibrium with pure condensed solvent. One should recall, however, the various approximations in deriving this expression. These tend to apply because the fractional changes in the lowering of the freezing point are small. Here we alter the earlier derivation by replacing the previously used $x_2 \approx -\ln(1 - x_2) = -\ln x_1$ with $x_2 \approx -\ln a_1(T, P, x_1)$ to write

$$-\ln a_1(T, P, x_1) = \frac{\tilde{L}_1 \Theta}{RT_f^2} + \left[\frac{\tilde{L}_1}{RT_f} - \frac{\tilde{C}_p^l - \tilde{C}_p^s}{2R} \right] \left(\frac{\Theta}{T_f} \right)^2 = -\ln \Gamma_1 - \ln x_1, \quad (3.7.1)$$

in which $\Theta \equiv T_0 - T_f$ represents the freezing point depression, \tilde{L}_1 is the molar heat of fusion of the pure solvent, and all other symbols retain their standard significance. One notes that when Θ has been experimentally determined, the activity coefficient $\Gamma_1(T, P, x_1)$ can be found.

Determination of Activity Coefficients at Temperatures Other than its Freezing Point

Equation (3.7.1) yields Γ_1 only at the freezing point T_f of the solution. To find the activity coefficient at some standard temperature T_s , introduce Eq. (3.5.2), so that $(\partial \ln \Gamma_1 / \partial T)_P = -(\bar{H}_1 - \tilde{H}_1^*) / RT^2$. Then,

$$\ln \frac{\Gamma_1(T_s)}{\Gamma_1(T_f)} = - \int_{T_f}^{T_s} \frac{\bar{H}_1 - \tilde{H}_1^*}{RT^2} dT \quad (\text{constant } P). \quad (3.7.2)$$

Here $\bar{H}_1 - \tilde{H}_1^*$ is the enthalpy difference in changing the solution from a pure state, $x = 1$, to a final composition x corresponding to temperature T_s . This difference must be known as a function of temperature T before the integration can be carried out. For this purpose, we next invoke *Kirchhoff's law*:

$$(\bar{H}_1 - \tilde{H}_1^*)_T = (\bar{H}_1 - \tilde{H}_1^*)_{T_f} + (\bar{C}_{1p} - \tilde{C}_{1p}^*)(T - T_f), \quad (3.7.3)$$

with which we obtain

$$\ln \frac{\Gamma_1(T_s)}{\Gamma_1(T_f)} = \frac{(\bar{H}_1 - \tilde{H}_1^*)_{T_f} (T_s - T_f)}{RT_s T_f} + [\bar{C}_{1p} - \tilde{C}_{1p}^* / R] [(T_s - T_f) / T_s - \ln(T_s / T_f)], \quad (3.7.4)$$

which solves the problem at hand. Note the many parameters that must be specified for use in this relation.

Activity of the Solute

If the activity of the solvent is known, that of the solute may be determined by using the relation

$$d \ln a_2(T, P, x_2) = -(x_1 / x_2) d \ln a_1(T, P, x_2). \quad (3.7.5)$$

To facilitate the calculations, normally carried out in terms of molality, we introduce Eq. (2.8.10a) to write ($x_1 \rightarrow 1$),

$$x_1 / x_2 = 1000 / m M_1 \equiv b_1 m, \quad (3.7.6)$$

where m is the molality of the solute, and M_1 is the gram molecular weight of the solvent. Also, we rewrite Eq. (3.7.1) in the obvious notation

$$-\ln a_1^{(x)} = -\ln a_1^{(m)} = b_2 \Theta + b_3 \Theta^2, \quad (3.7.7)$$

in which b_2 and b_3 are the multipliers of Θ and of Θ^2 in Eq. (3.7.1). Now execute a differentiation of the above to find

$$-d \ln a_1^{(m)} = (b_2 + 2b_3 \Theta) d\Theta, \quad (3.7.8)$$

so that Eq. (3.7.5) may be rewritten as

$$d \ln a_2^{(m)} = (b_1/m)(b_2 + 2b_3\Theta)d\Theta \equiv d\Theta/\lambda m + c\Theta d\Theta/m, \quad (3.7.9)$$

with $\lambda^{-1} \equiv b_1b_2$ and $c \equiv 2b_1b_3$. In further manipulations, it is convenient to introduce a quantity

$$j \equiv 1 - \Theta/\lambda m \quad (3.7.10)$$

so that

$$dj = -d\Theta/\lambda m + (\Theta/\lambda m^2)dm = -d\Theta/\lambda m + (\Theta/\lambda m)d \ln m = -d\Theta/\lambda m + (1-j)d \ln m, \quad (3.7.11a)$$

or

$$d\Theta/\lambda m = (1-j)d \ln m - dj. \quad (3.7.11b)$$

Now insert Eq. (3.7.11b) into Eq. (3.7.9). At this stage, we introduce $\Gamma_2^{(m)}$ as the activity coefficient when molality m is used as concentration variable. Then

$$d \ln \Gamma_2^{(m)} = d \ln a_2^{(m)} - d \ln m = -jdm/m - dj + c\Theta d\Theta/m. \quad (3.7.12)$$

We next integrate from very dilute solutions, $m=0$, to a final value m . For very dilute solutions, Eq. (3.7.7) reads $-\ln x_1 = b_2\Theta = -\ln(1-x_2) \approx x_2 \approx x_2/x_1 \approx m/b_1$. It then follows from Eq. (3.7.10) that $j=0$ for $m=0$. The integration over m of Eq. (3.7.12) thus yields the final desired result ($\ln \Gamma_2^{(m)}$ vanishes at infinite dilution):

$$\ln \Gamma_2^{(m)}(T_f) = 1 - \Theta/\lambda m - \int_0^m (j/m)dm + c \int_0^m (\Theta/m)d\Theta. \quad (3.7.13)$$

The integrations can be executed numerically after the freezing point depression Θ has been determined empirically as a function of the molality m . This then yields the activity coefficient of the solute at the freezing point of the solution.

Activity Coefficient of Solute at Arbitrary Temperatures

To find the activity coefficient $\Gamma_2^{(m)}$ at a standard temperature T_s other than the freezing point, we set

$$y \equiv \ln \left[a_1^{(m)}(T_s)/a_1^{(m)}(T_f) \right], \quad (3.7.14)$$

whence

$$d \ln a_2^{(m)}(T_s) = -(x_1/x_2)d \ln a_1^{(m)}(T_s) = -(x_1/x_2)d \ln a_1^{(m)}(T_f) - (x_1/x_2)dy. \quad (3.7.15)$$

We now let $x_1/x_2 = b_1/m$, Eq. (3.7.6), and determine the quantity

$$d \ln \Gamma_2^{(m)}(T_s) = d \ln a_2^{(m)}(T_s) - d \ln m = -(b_1/m)d \ln \left[a_1^{(m)}(T_f) \right] - (b_1/m)dy - d \ln m. \quad (3.7.16)$$

This expression correlates $\gamma_2^{(m)}$ at the standard temperature T_s with the activity of the solvent $a_1^{(m)}$ at the freezing point of the solution. Next, at $T=T_f$ let us set $-(b_1/m)d \ln a_1^{(m)} = d \ln a_2^{(m)}$ to obtain

$$d \ln \Gamma_2^{(m)}(T_s) = d \ln \left[a_2^{(m)}(T_f) \right] - d \ln m - (b_1/m)dy = d \ln \Gamma_2^{(m)}(T_f) - (b_1/m)dy. \quad (3.7.17)$$

Next, integrate from $m = 0$ to m . At the lower limit, $\Gamma_2^{(m)} = 1$, so that its logarithm vanishes. We obtain

$$\ln \Gamma_2^{(m)}(T_s) = \ln \Gamma_2^{(m)}(T_f) - b_1 \int_0^m (1/m)dy, \quad (3.7.18)$$

which is the final desired relation. The variation of m with y must be determined empirically, generally a laborious procedure.

Elevation of the Boiling Point

Procedures analogous to the above apply to the determination of activities from the boiling point elevation. The requisite changes in the derivations should be fairly obvious and will not be detailed here.

Comment

This concludes the discussions of how one may determine the activities or activity coefficients of materials constituting real solutions, thereby enlarging on the thermodynamic theory of ideal solutions.

3.8 Thermodynamic Properties of Nonideal Solutions

Here we study the formation of a nonideal solution from its pure constituents; these results should be contrasted with those of Section 2.5. As we do this, notice how many of our deductions rest on the very simple approach introduced here—an excellent illustration of the power of systematized thermodynamics.

All thermodynamic properties of interest in the present study will be derived from the Gibbs free energy of mixing, namely

$$\Delta G_m = \sum_{i=1}^c n_i [\mu_i(T, P, x_i) - \mu_i^*(T, 1)], \quad (3.8.1)$$

in which μ_i is the chemical potential of constituent i in the nonideal solution, whose composition is specified by mole numbers n_i and mole fraction x_i , and $\mu_i^*(T, 1)$ is the corresponding chemical potential of each constituent in its pure form at the same temperature and at a pressure of 1 bar.

Thermodynamic Functions of Mixing

We begin by introducing Eq. (3.3.9) into Eq. (3.8.1) to write

$$\Delta G_m = RT \sum_i n_i \ln [\Gamma_i(T, P, x_i)x_i]. \quad (3.8.2)$$

From Eq. (3.8.2), we readily obtain

$$\Delta S_m = -\left(\partial \Delta G_m / \partial T\right)_{P, x_i} = -R \sum_i n_i \ln(\Gamma_i x_i) - RT \sum_i n_i (\partial \ln \Gamma_i / \partial T)_{P, x_i} \quad (3.8.3)$$

$$\Delta H_m = -T^2 (\partial \Delta G_m / \partial T)_{P, x_i} = -RT^2 \sum_i n_i (\partial \ln \Gamma_i / \partial T)_{P, x_i} \quad (3.8.4)$$

$$\Delta V_m = (\partial \Delta G_m / \partial P)_{T, x_i} = RT \sum_i n_i (\partial \ln \Gamma_i / \partial P)_{T, x_i} \quad (3.8.5)$$

$$\Delta E_m = \Delta H_m - P \Delta V_m \quad (3.8.6)$$

$$\Delta C_P|_m = -RT \sum_i n_i \left[2(\partial \ln \Gamma_i / \partial T)_{P, x_i} + T(\partial^2 \ln \Gamma_i / \partial T^2)_{P, x_i} \right]. \quad (3.8.7)$$

A corresponding equation is obtained for $C_V|_m$. The various partial derivatives called for in Eqs. (3.8.3)–(3.8.7) may be determined via Eqs. (3.5.1) and (3.5.2). The above expressions all properly reduce to the results of Section 2.5 for ideal solutions.

Mixing in Binary Solutions; the Margules Equation

We examine Eq. (3.8.2) in greater detail for a binary solution. Set $\Delta \tilde{G}_m = \Delta G_m / (n_1 + n_2)$, so as to achieve a symmetric formulation

$$(\Delta \tilde{G}_m) / RT = x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln \Gamma_1 + x_2 \ln \Gamma_2. \quad (3.8.8)$$

We now need explicit relations for Γ_1 and Γ_2 . The simplest useful procedure involves an expansion of $\ln \Gamma_1$ and of $\ln \Gamma_2$ in a power series in x_1 and x_2 as follows:

$$\ln \Gamma_1 = \ln a_1 - \ln x_1 = D_1 x_2 + B_1 x_2^2 + \cdots \quad (3.8.9a)$$

$$\ln \Gamma_2 = \ln a_2 - \ln x_2 = D_2 x_1 + B_2 x_1^2 + \cdots \quad (3.8.9b)$$

Note that $\ln \Gamma_1$ is expanded as an ascending power series in x_2 and $\ln \Gamma_2$, in an ascending series in x_1 . This ensures that when $x_2 \rightarrow 0$, $\Gamma_1 \rightarrow 1$ and when $x_1 \rightarrow 0$, $\Gamma_2 \rightarrow 1$, as required. The series (3.8.9) as written will be useful if, for successive members $C_1 x_2^3 + F_1 x_2^4 + \cdots$ the inequality $|C_1|, |F_1|, \dots \ll |B_1|$ applies.

The coefficients on the right of Eqs. (3.8.9) are not arbitrarily adjustable, as is seen by solving Eqs. (3.8.9) for $\ln a_i = \ln ax_i + D_i(1 - x_i) + B_i(1 - x_i)^2$, with $i = 1, 2$, and then constructing the expression

$$x_i d \ln a_i = x_i d \ln x_i - (D_i + 2B_i)x_i dx_i + 2B_i x_i^2 dx_i, \quad (3.8.10)$$

Next, from Eq. (3.8.10) form the sum $x_1 d \ln a_1 + x_2 d \ln a_2$ which at constant T and P must be made to vanish, so as to satisfy the Gibbs–Duhem relation. Also, note that $x_1 d \ln x_1 + x_2 d \ln x_2 = dx_1 + dx_2$. By setting $i = 1, 2$ and adding the two expressions, we obtain

$$0 = dx_1 + dx_2 - (D_1 + 2B_1)x_1 dx_1 - (D_2 + 2B_2)x_2 dx_2 + 2B_1 x_1^2 dx_1 + 2B_2 x_2^2 dx_2. \quad (3.8.11a)$$

Now set $x_2 = 1 - x_1$ and $dx_2 = -dx_1$, cancel out the common multiplier dx_1 , and rearrange the resulting term in ascending powers of x_1 . This yields

$$D_2 - [D_1 + D_2 + 2(B_1 - B_2)]x_1 + 2(B_1 - B_2)x_1^2 = 0. \quad (3.8.11b)$$

The coefficients of $x_1^0 = 1, x_1^1, x_1^2, 1^2$ must vanish separately if Eq. (3.8.11b) is to vanish for arbitrary x_1 in the interval $0 \leq x_1 \leq 1$. This requirement is met by setting $D_1 = D_2 = 0$ and $B_2 = B_1 = B$, which leads via Eqs. (3.8.9) directly to the *Margules* (1895) equations:

$$\ln \Gamma_1 = Bx_2^2; \quad \ln \Gamma_2 = Bx_1^2. \quad (3.8.12a)$$

or

$$\Gamma_1 = \exp(Bx_2^2); \quad \Gamma_2 = \exp(Bx_1^2). \quad (3.8.12b)$$

On introducing Eq. (3.8.12a), Eq. (3.8.8) assumes the form

$$\Delta G_m / RT = x_1 \ln x_1 + x_2 \ln x_2 + Bx_1x_2. \quad (3.8.13)$$

This is a fundamental equation that forms the bed rock of much of our subsequent discussion.

Pictorial Representations of the Margules Relations

We note that for ideal solutions, $B = 0$, for which the variation of $\Delta \tilde{G}_m / RT$ with x_2 is represented by curve 1 in Figure 3.8.1. Since $x_1, x_2 < 1$, $\Delta \tilde{G}_m$ is necessarily negative: thus, the mixing process for components to form a homogeneous solution occurs spontaneously. For $B < 0$, the term Bx_1x_2 renders $\Delta \tilde{G}_m$ even more negative than for the ideal case; this situation is represented by Curve 5 in the diagram. However, a very interesting situation arises for $B > 0$; for, when B becomes sufficiently large, the simple monotonic variation of $\Delta \tilde{G}_m$ with $x_2 \equiv x$ gives way to a more complex behavior: with increasing x , $\Delta \tilde{G}_m$ diminishes to a first local minimum, then rises to an absolute maximum in at $x = 1/2$, followed by another minimum and a rise to zero at $x = 1$. As are the other curves, this one is symmetric about $x = 1/2$. This situation is depicted by curve 4 on the diagram. Curve 3 is discussed later.

Phase Separation

We now touch on a point that addresses the problem of phase separation, which is rendered possible when $B > 0$. Reference is made to curve 4 of Figure 3.8.1, which is redrawn in Figure 3.8.2, where we set $x \equiv x_2$. Note the symmetrically displayed minima in $\Delta \tilde{G}_m$ that occur at mole fractions x' and x'' . If the solution were homogeneous over the entire x range, the reduced free-energy curve would apply to the entire range of x and show the indicated rise and fall with x for $x' < x < x''$. However, this part of the curve lies above the straight (dashed) line which results if one were to form a *heterogeneous* mixture from appropriate amounts of constituents of the fixed compositions x' and x'' . Hence, the heterogeneous mixture is the stable one in this range. As an example, the midpoint corresponds to the case wherein the solution breaks down into equal amounts of material of composition x' and x'' as constituting the heterogeneous mixture. The nature of the heterogeneous phase for other x values is discussed below. It is thus implicit that no homogeneous solution can exist within the range $x' < x < x''$; the two-phase mixture is always more stable than the homogeneous phase would have been.

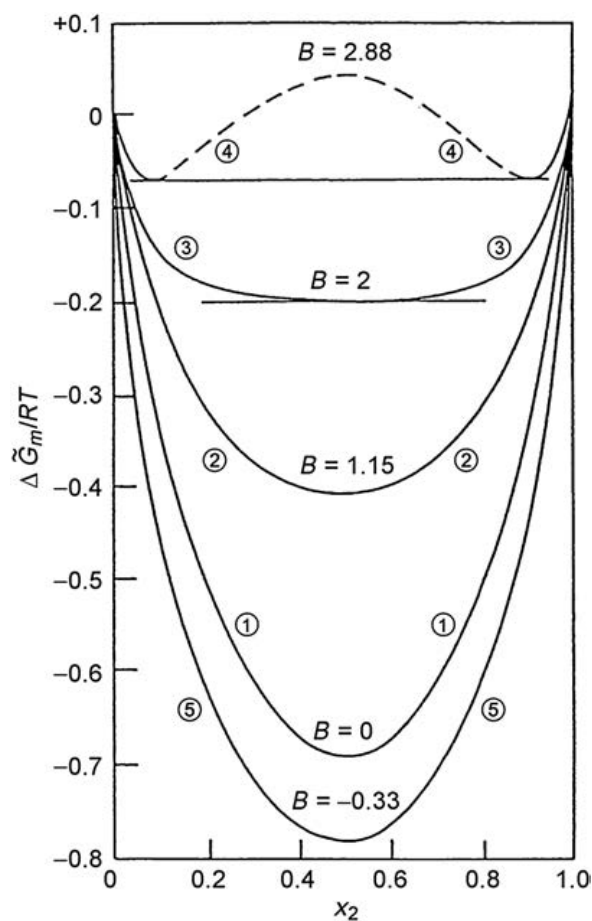


FIGURE 3.8.1

The Gibbs free energy of mixing of two components in a nonideal solution, as specified by Eq. (3.8.13) for various values of B .

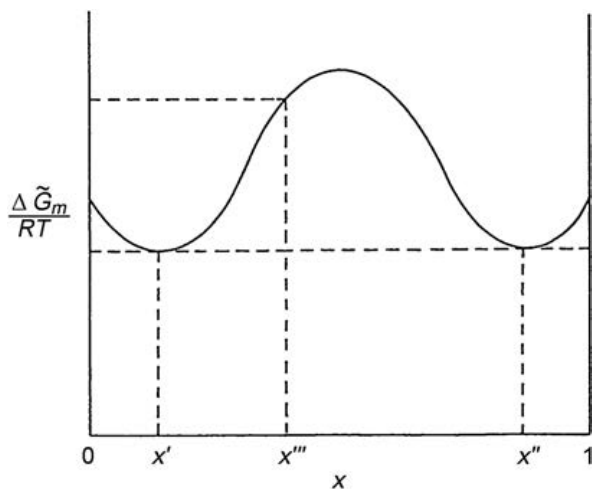


FIGURE 3.8.2

Illustration showing the reduction in the reduced Gibbs free energy of mixing when a mixture of mole fraction x''' splits into two phases of composition x' and x'' in mutual equilibrium.

Again, since $\Delta\tilde{G}_m$ is reduced through separation of the solution into two distinct phases, so as to render $\Delta\tilde{G}_m$ as small as possible, such a process occurs spontaneously. Stated differently, the putative homogeneous solution splits into two components, x' and x'' , whose compositions correspond to the minima of the curve; the two distinct phases $x = x'$ and $x = x''$ are in mutual equilibrium.

The specific compositions x' and x'' of the heterogeneous phases may be determined through the requirement that x be a minimum at these two points: $(\partial\Delta\tilde{G}_m/\partial x) = 0$. Because of the symmetry inherent in Eq. (3.8.13), $x' = 1 - x''$. On setting $x_1 = x_2 = x = 1 - x_1$ in Eq. (3.8.13) and then setting $(\partial\Delta\tilde{G}_m/\partial x)_T/RT$ one arrives at

$$\ln[x''/1 - x''] = B(2x'' - 1), \quad (3.8.14)$$

which is a transcendental equation that must be solved numerically for $x = x''$ once B is specified. As B is increased, x' and x'' move symmetrically away from the value $1/2$ toward the values 0 and 1, respectively; for, as $B \rightarrow \infty$, in Eq. (3.8.14), x'' must approach unity.

Also, as is seen from Figure 3.8.1, there exists a critical B value, B_c , for which $x' = x'' = 1/2$; when $B < B_c$, no phase separation is encountered. The critical value B_c (which separates the U-shaped curves from those that have their minima away from $x = 1/2$) is determined from two requirements that must be imposed on Eq. (3.8.13):

$$\partial^2\Delta G_m/\partial x^2 = 0 = 1/(1 - x_c) + 1/x_c - 2B_c \quad (3.8.15a)$$

and

$$\partial^3\Delta G_m/\partial x^3 = 0 = 1/(1 - x_c)^2 - 1/x_c^2. \quad (3.8.15b)$$

These two equations lead to the solution

$$x_c = \frac{1}{2}, \quad B = 2. \quad (3.8.15c)$$

The corresponding variation of $\Delta\tilde{G}_m/RT$ with x_2 is shown as curve 3 in Figure 3.8.1.

The very simple model introduced here provides a semiquantitative framework for understanding the origin of phase separation phenomena in real binary solutions.

Fugacity of Gas Phases

We can go further by examining the constitution of the gas phase in equilibrium with a nonideal solution containing a volatile constituent. We return briefly to Eqs. (3.8.9) which becomes (with $D = 0$, $B_1 = B_2 \equiv B$)

$$\ln a_1 = \ln x_1 + Bx_2^2. \quad (3.8.16)$$

Plots of a_1 vs x_1 are shown in Figure 3.8.3 for $B = 0, 1.15, 2, 2.88$. One notes that for $B > B_c = 2$, there exist two values of x_1 , namely x'_1 and x''_1 that are associated with the same activity. Since $\mu_1 = \mu_1^* + RT \ln a_1 + RT \ln a_1$, the equality $a_1(x'_1) = a_1(x''_1)$ implies an equality of chemical potentials: $\mu_1(x'_1) = \mu_1(x''_1)$, that is again an indication of two discrete phases of composition x'_1 and x''_1 in mutual equilibrium.

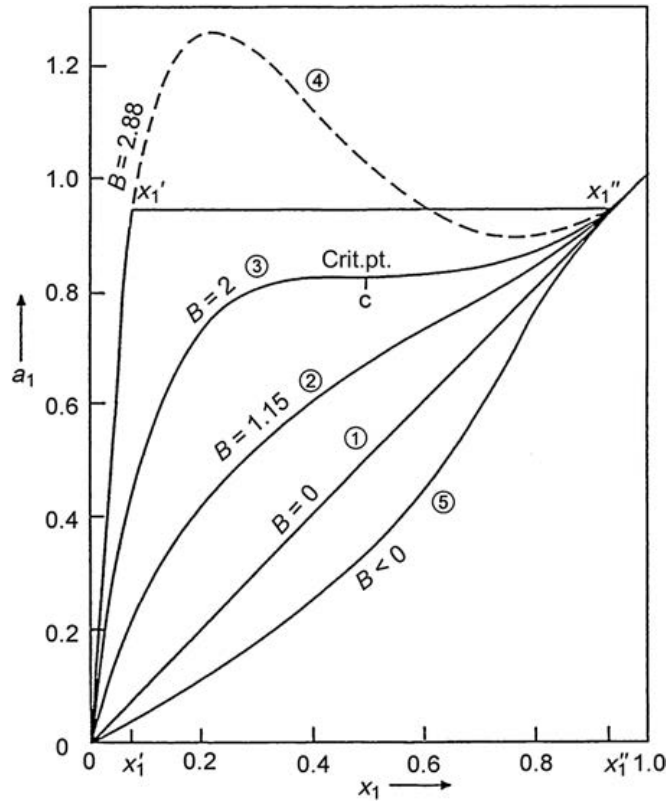


FIGURE 3.8.3

Activity of component 1 vs mole fraction x_1 in a binary mixture, as determined by Eq. (3.8.16).

Note that Figure 3.8.3 is also representable as a vapor pressure diagram of P_1/P_1^* vs x_1 . For, when equilibrium prevails, we require that $\mu_1^* + RT \ln a_1 = \mu_1^{OP} + RT \ln P_1$ on setting $a_1 = \Gamma_1 x_1$ and rearranging, we find $x_1 \Gamma_1 / P_1 = a_1 / P_1 = \exp[\mu_1^{OP} - \mu_1^* / RT] \equiv C$. For pure liquid 1, $x_1 = 1$, $\Gamma_1 \approx a_1 = 1$, $P_1 = P_1^*$ thereby rendering $C = 1/P_1^*$, so that finally $P_1/P_1^* = a_1$, which proves the assertion. Thus, Figure 3.8.3 is equivalent to the standard diagrams that show departures from Raoult's Law. The interpretation of curve 4 on the diagram now runs as follows: as the solution is rendered increasingly rich in component 1, the partial pressure of component 1 in the vapor phase rises much more rapidly than would be the case for an ideal solution. In the range $x_1' \leq x_1 \leq x_1''$, P_1/P_1^* remains fixed, corresponding to the fact that there now exist three phases in mutual equilibrium, i.e., two liquids and the vapor. As the solution is made increasingly rich in component 1, the condensed phase of composition x_1'' grows at the expense of the phase at composition x_1' . Ultimately, for compositions $x_1 > x_1''$, one reverts back to a single liquid phase, and P_1 again varies with x_1 until the value $P_1 = P_1^*$ is reached at $x_1 = 1$. Note further that as $x_1 \rightarrow 1$, all curves in Figure 3.8.3 merge with the one for which $B = 0$; this agrees with the experimental fact that Raoult's Law always holds in this range. Similarly, as $x_1 \rightarrow 0$, one obtains a straight-line region consistent with Henry's Law; here as $x_1 \rightarrow 0$, the slope varies with each solution. For $B < 0$ negative deviations from Raoult's Law are encountered, but for $B > 0$ one finds positive deviations with slopes that become steeper, the greater the positive departure from ideality.

It is remarkable how such a simple model as the above can rationalize so many experimental observations.

Entropy of Solution

Finally, we note an important point: as long as B is taken to be independent of T , the term $-R(x_1 \ln x_1 + x_2 \ln x_2)$, Eq. (3.8.13) represents the entropy of mixing, which, in this approximation is the same as for an ideal solution. The term Bx_1x_2 is then to be identified with $\Delta\tilde{H}_m = \Delta\tilde{G}_m + T\Delta\tilde{S}_m$. We may then rewrite Eq. (3.8.13) as

$$\Delta\tilde{H}_m = RTBx_1x_2 = wx_1x_2, \quad (3.8.17)$$

in which we have set $B \equiv w/RT$ and where we introduce $\Delta\tilde{H}_m = RTB_{x_1x_2} = wx_1x_2$. On using the definitions for mole fraction, we obtain $[\Delta G = n\Delta\tilde{G} = n\Delta\tilde{G} = (n_1 + n_2)\Delta\tilde{G}]$

$$\Delta G_m = RT\{n_1 \ln x_1 + n_2 \ln x_2\} + wn_1n_2/n, \quad (3.8.18)$$

with $w = w(T)$. Clearly, in this oversimplified model, all of deviations from ideality are to be associated with the presence of a nonzero enthalpy of mixing term, namely $w(n_1n_2/n)$.

Several *ad hoc* methods have been proposed to simulate a contribution of the entropy to nonideality while retaining the present model. In the simplest representation, one allows the coefficient B in Eq. (3.8.13) to be a function of T , $B = B(T)$. One can readily check that (w' represents the temperature derivative)

$$\Delta\tilde{S}_m = -\partial\Delta\tilde{G}_m/\partial T = -R\{x_1 \ln x_1 + x_2 \ln x_2\} - (\partial w/\partial T)x_1x_2, \quad (3.8.19)$$

is the molar entropy of mixing, which is still symmetric in the 2 mol fractions but does add a correction term to the ideal molar entropy of mixing. The molar enthalpy of mixing is then $\partial(\Delta\tilde{G}_m/T)/\partial T = -\Delta\tilde{H}_m/T^2$, yielding

$$\Delta\tilde{H}_m = (w - w'T)x_1x_2, \quad (3.8.20)$$

which is still a symmetric, but now T -dependent, quantity. Usually w' is of the order of $10^{-2}w$, but, when multiplied by generally prevalent values of T , is of order w and hence not negligible in Eq. (3.8.20).

Asymmetric Mixing Functions

So far the mixing terms have been strictly symmetric with respect to an interchange of the designations of components 1 and 2. This is scarcely the case in real life. A version of asymmetry is introduced by requiring that the free energy of mixing have the form, termed the *Flory–Huggins model*,

$$G - G^* = RT[n_1 \ln \phi_1 + n_2 \ln \phi_2] + \hat{A}(T)(n_1\tilde{V}_1^0 + n_2\tilde{V}_2^0)\phi_1\phi_2, \quad (3.8.21a)$$

Here, we introduced $\hat{A}(T)$ as an interaction energy parameter, and used the definition

$$\phi_i \equiv \frac{n_i\tilde{V}_i^0}{n_1\tilde{V}_1^0 + n_2\tilde{V}_2^0}, \quad (i = 1, 2) \quad (3.8.21b)$$

in which the \tilde{V}_i^0 are the molar volumes of component i in pure form. We shall neglect the temperature and pressure dependence of these quantities.

The above formulation for the free energy of formation of the solution satisfies two important criteria. First, it must be checked whether the chemical potentials satisfy the requirement $G = n_1\mu_1 + n_2\mu_2$. The required chemical potentials are found by differentiation of Eqs. (3.8.21)—a straightforward though quite tedious analysis. One finds that

$$(\mu_1 - \mu_1^*)/RT = \ln \varphi_1 + \left[(\tilde{V}_2^0 - \tilde{V}_1^0) / \tilde{V}_2^0 \right] \varphi_2 + \hat{A}(T) \tilde{V}_2^0 \varphi_2^2 / RT, \quad (3.8.22)$$

with a similar expression for the second component, in which the subscripts 1 and 2 are interchanged. Although not obvious, the chemical potentials so found do meet the stipulated condition. Second, it must be verified that the Gibbs–Duhem relation $n_1 d\mu_1 + n_2 d\mu_2 = 0$ is satisfied. To show that this is the case is another very tedious exercise in standard calculus. I gladly leave to you the tedium of checking the above assertions. The formulation (3.8.21) does indeed obey the sufficient conditions for a particular, correct representation of the Gibbs free energy of nonideal solutions.

From Eq. (3.8.21a), one obtains the following expressions: by differentiation with respect to T , the entropy of mixing is specified by

$$S - S^* = -R(n_1 \ln \varphi_1 + n_2 \ln \varphi_2) - (n_1 \tilde{V}_1^0 + n_2 \tilde{V}_2^0) \varphi_1 \varphi_2 d\hat{A}(T)/dT, \quad (3.8.23a)$$

and the enthalpy of mixing, as derived in the manner of Eq. (3.8.20), is given by

$$H - H^* = (n_1 \tilde{V}_1^0 + n_2 \tilde{V}_2^0) \varphi_1 \varphi_2 \left[\hat{A}(T) - T d\hat{A}(T)/dT \right]. \quad (3.8.23b)$$

It is easy to establish that Eqs. (3.8.21) and (3.8.23) may be converted to molar form by replacing all n_i with x_i . The resulting expressions, considered as a function of x_1 and x_2 , are clearly asymmetric in the 2 mol fractions. In actual calculations, it is expedient to introduce the ratio $r_1 \equiv \tilde{V}_1^0 / \tilde{V}_2^0$ and to set $\tilde{V}_1^0 \hat{A}(T) \equiv C(T)$. Eq. (3.8.21a) then reduces to a form that involves the asymmetry parameter r along with C :

$$\Delta \tilde{G}_m = RT[x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln r_1 - \ln(r_1 x_1 + x_2)] + C(T) \frac{x_1 x_2}{r_1 x_1 + x_2}, \quad (3.8.24)$$

from which one obtains in the customary manner

$$\Delta \tilde{S}_m = -R[x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln r_1 - \ln(r_1 x_1 + x_2)] - C'(T) \frac{x_1 x_2}{r_1 x_1 + x_2}, \quad (3.8.25)$$

and

$$\Delta \tilde{H}_m = [C(T) - TC'(T)] \frac{x_1 x_2}{r_1 x_1 + x_2}. \quad (3.8.26)$$

The asymmetries are now present in both the entropic and enthalpic contributions. The above correctly reduce to Eqs. (3.8.13), (3.8.19) and (3.8.20) when $r_1 = 1$. One may obtain the heat capacity contribution by differentiation of Eq. (3.8.26) with respect to temperature.

Calculations based on the use of the above relations will be briefly described in the next section.

Summary

It is quite remarkable how many firm deductions have been based on a single hypothesis. Starting with the Margules formulation (3.8.12) for Γ_i , thermodynamics leads directly to the specification of $\Delta \tilde{G}_m$,

as shown in Eq. (3.8.13). All other mixing functions are then found from Eqs. (3.8.3)–(3.8.7) or Eqs. (3.8.24)–(3.8.26). When phase separation does occur, the composition of the two phases in equilibrium is specified by Eq. (3.8.14); the analogous relation for the asymmetric version gets to be complicated and is best arrived at via numerical solutions.⁶ The critical value of B required for incipient phase separation, and the critical composition of the mixture are specified⁶ by Eq. (3.8.15c). Finally, one may construct diagrams such as shown in Figure 3.8.3 by which deviations from Raoult's Law are predicted.

Exercises

- 3.8.1.** Try to “improve upon” the Margules model by including a cubic term in the expansion of Eqs. (3.8.9a,b), and note the resulting complications.
- 3.8.2.** Derive expressions for $\Delta\tilde{S}_m/RT$, $\Delta\tilde{H}_m/RT$, $\Delta\tilde{E}_m/RT$ assuming that w is a constant. Sketch the resulting curves for $B = -1, 0, 1.5, 3$ at $T = 300$ K and comment on the nature of your results.
- 3.8.3.** For certain types of high polymer solutions, the chemical potentials of (1) the solvent and (2) solute are given by the approximate relations,

$$\tilde{G}_1 = \tilde{G}_1^0(T, P) + RT[\ln \varphi_1 + (1 - 1/r)\ln(1 - \varphi_1)] + w(1 - \varphi_1)^2,$$

$$\tilde{G}_2 = \tilde{G}_2^0(T, P) + RT[\ln \varphi_2 - (r - 1)\ln(1 - \varphi_2)] + rw(1 - \varphi_2)^2,$$

$$\varphi_1 \equiv N_1/(N_1 + rN_2); \quad \varphi_2 \equiv rN_2/(N_1 + rN_2).$$

Here N_1 and N_2 are the number of solvent and solute molecules, respectively. Each polymer is assumed to consist of r monomers, and the volumes of each monomer and each solvent molecule are assumed to be roughly equal. (a) Relate φ_1 and φ_2 to x_1 and x_2 . (b) Determine the entropy of mixing and compare the result with that for an ideal solution. (c) Determine the enthalpy of mixing and compare it to the Margules formulation.

- 3.8.4.** It is found empirically that the vapor pressure of component 2 nonideal solution may be specified by $P_2 = (2x_2 - x_2^2)P_2^*$. (a) Determine its activity coefficient relative to the standard state. (b) Find an analytic expression for P_1 in terms of x_1 . (c) Plot out the partial pressures as a function of composition and note their shape.
- 3.8.5.** Prove that Eq. (3.8.22) and its counterpart for the second component do together satisfy the relation $G = n_1\mu_1 + n_2\mu$ and the Gibbs–Duhem relation. Note in this connection that φ_1 and φ_2 both involve n_1 and n_2 . The derivations are straightforward but tedious.
- 3.8.6.** Derive relations that specify the compositions x' and x'' for the Flory–Huggins model. Also determine the critical value of the interaction parameter for phase separation.

Phase Stability: General Consequences of Deviations from Ideality

We had earlier initiated a discussion showing how deviations from ideal behavior of binary solutions led to the phenomenon of phase separation (cf. the discussion following the Margules relation). We

now introduce several generalizations on the basis of qualitative sketches introduced below. This sets the stage for the discussion on phase diagrams, to follow.

In ideal solutions, the mixing process is rendered spontaneous through the positive entropy of mixing $\Delta\tilde{S}_m/R = -\{x_1 \ln x_1 + x_2 \ln x_2\} > 0$; here $\Delta\tilde{H}_m = 0$. The molar free energy for ideal solutions reads

$$\tilde{G} = RT\{x_1 \ln x_1 + x_2 \ln x_2\} + (x_1\mu_1^* + x_2\mu_2^*) \quad (3.8.27a)$$

$$\tilde{G} = -T\Delta\tilde{S}_0 + \tilde{G}^*. \quad (3.8.27b)$$

Qualitatively, Eq. (3.8.1) may be represented as shown in Figure 3.8.4(b), where energy is plotted schematically vs $x_2 \equiv x$. The figure plots $-T\Delta\tilde{S}_0$ vs x as the bottom curve; the sloping baseline (top curve) for \tilde{G}^* is obtained from the sum $x_1\mu_1^* + x_2\mu_2^*$ in which the μ_i^* are held fixed. The resultant graph, shown in the middle, $\tilde{G} = -T\Delta\tilde{S} + \tilde{G}^*$, is a skewed U-shaped curve. For nonideal solutions, two corrections are inserted: (i) an excess entropy term \tilde{S}_e must be added to $\Delta\tilde{S}_0$ to account for deviations from ideality, as in Eq. (3.8.19). The result may be simulated by the expression $\Delta\tilde{S} = x_1 \ln x_1 + x_2 \ln(rx_2)$ where r is a suitable parameter. One now obtains a skewed $-T\Delta\tilde{S}$ curve of the type shown in Figure 3.8.4(a) and (c). (ii) Also, the enthalpy of mixing no longer vanishes but varies with $x_2 \equiv x$ which is simulated by $\Delta\tilde{H} = wx(1-x)/[1+(r-1)x]$ of Eq. (3.8.26), and which reduces to the last term of Eq. (3.8.17) when $r = 1$. On introducing these corrections, one obtains a new curve, sketched in part (a) where $w < 0$, and in part (c) where $w > 0$. The resultants obtained on adding up the sloping baselines, the entropy, and the enthalpy contributions are indicated by curve \tilde{G} . In part (a), \tilde{G} is simply more negative and more skewed than for part (b), but in part (c), a nonmonotonic variation of \tilde{G} with x is obtained, because over certain ranges of x , large positive $\Delta\tilde{H}$ values outweigh the negative contributions associated with $-T\Delta\tilde{S}$. As already indicated earlier, and as will again be shown shortly, such a situation signals the onset of phase separation.

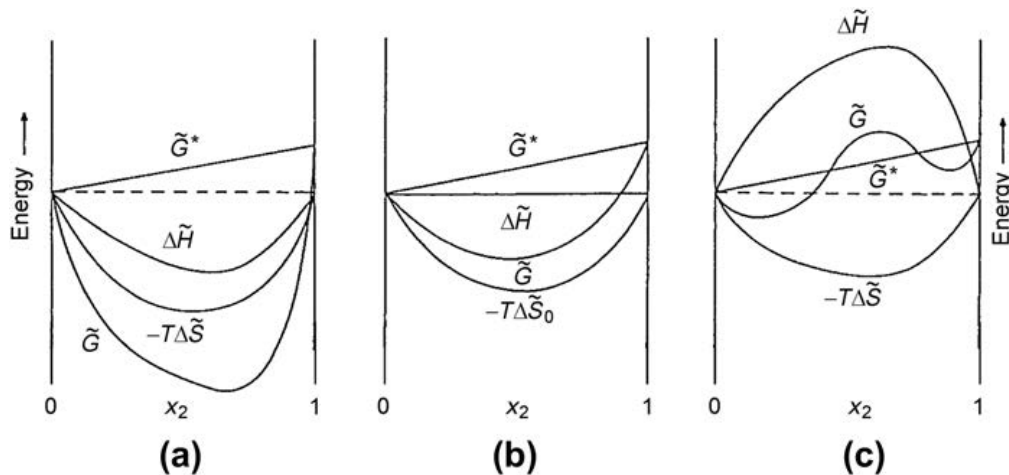


FIGURE 3.8.4

Schematic representations of several (free) energies of binary solutions under various assumed conditions: (a) $\Delta\tilde{H} < 0$, (b) $\Delta\tilde{H} = 0$, (c) $\Delta\tilde{H} > 0$. Note the nonmonotonic change of \tilde{G} in the latter case.

The Lever Rule

We now establish how much of each phase must be present to form a heterogeneous mixture of average mole fraction x . You should consult Table 3.8.I, in deriving the so-called lever rule.

Consider $n = n_A + n_B$ moles of A and B with an overall mole fraction $1 - x \equiv n_A/n$. Let a two-phase mixture be formed such that the mole fraction of A in the first phase and in the second phase is given by $1 - x' = n'_A/(n'_A + n'_B)$ and $1 - x'' = n''_A/(n''_A + n''_B)$, respectively. Let the fraction of the

Table 3.8.I Compositional Relations for Binary Mixtures

Phase'	Phase''
Mole fractions, total	
$n_A = (1 - x)n$	$n_B = nx$
Mole numbers	
n'_A, n'_B	n''_A, n''_B
Mole fractions	
$x'_A = \frac{n'_A}{n'_A + n'_B} \equiv 1 - x'$	$x''_A = \frac{n''_A}{n''_A + n''_B} \equiv 1 - x''$
$x'_B = \frac{n'_B}{n'_A + n'_B} \equiv x'$	$x''_B = \frac{n''_B}{n''_A + n''_B} \equiv x''$
Total mole numbers per phase	
$n' = n'_A + n'_B$	$n'' = n''_A + n''_B$
Mole fraction for each phase	
$1 - f = \frac{n'}{n' + n''} = \frac{n'}{n}$	$f = \frac{n''}{n' + n''} = \frac{n''}{n}$
Overall composition of system	
$x_A = \frac{n_A}{n_A + n_B} = \frac{n_A}{n} = 1 - x$	$x_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n} = x$
Conservation of mole numbers	
$n_A = n'_A + n''_A$	$n_B = n'_B + n''_B$
Interrelations of mole fractions	
$(1 - x)n = (1 - x')n' + (1 - x'')n''$ $= (1 - x')(1 - f)n + (1 - x'')fn$	$xn = x'n' + x''n''$ $= x'(1 - f)n + x''fn$
Final interrelations	
$n_A = n(1 - x)$	$n_B = nx$
$n' = n(1 - f)$	$n'' = nf$
$n'_A = n'(1 - x')$	$n''_A = n''(1 - x'')$
$n'_B = n'x'$	$n''_B = n''x''$

total mole numbers in the ' phase be $1 - f \equiv (n'_A + n'_B)/n$. Then $n_A = n(1 - x)$, $n'_A = n(1 - f)(1 - x')$ and $n''_A = nf(1 - x'')$. Conservation of mole numbers requires that $n_A = n'_A + n''_A$. On substituting and solving for f , one obtains

$$f = (x - x')/(x'' - x') \quad (3.8.28a)$$

$$1 - f = (x'' - x)/(x'' - x') \quad (3.8.28b)$$

which results are known as the *Lever Rule*.

Homogeneous vs Heterogeneous Solutions

For a given set of conditions, can one predict whether a given alloy or solution is homogeneous or not? Consider a solution of mole fraction x_0 for a system for which Figure 3.8.5 is relevant. If the alloy were simply a mechanical mixture of the pure components A and B, then according to the Lever Rule, the free energy of the system would be given by the intersection \tilde{G}^* of the straight line joining \tilde{G}_A^* to \tilde{G}_B^* with the vertical line at $x = x_0$. If instead the phase mixture involved two solutions of compositions x'_a and x''_a , then the same Lever Rule yields the free energy of the alloy designated as \tilde{G}_a . Since $\tilde{G}_a < \tilde{G}^*$ this new state is more stable than the original one. Analogous remarks apply to another heterogeneous alloy whose two compositions are represented by x'_b and x''_b ; the corresponding free energy, \tilde{G}_b , is still lower. Continuing this process, it is found that at the composition x where the two phases merge into a single homogeneous solution of composition x_0 , the free energy attains its lowest possible value, \tilde{G}_0 . This is the stable configuration. For the type of free energy displayed in Figure 3.8.5, a straight line joining any two points on the curve always lies above the points on the curve between the intersection points. When the free energy vs composition curve is U shaped, the homogeneous solution always has the lowest free energy.

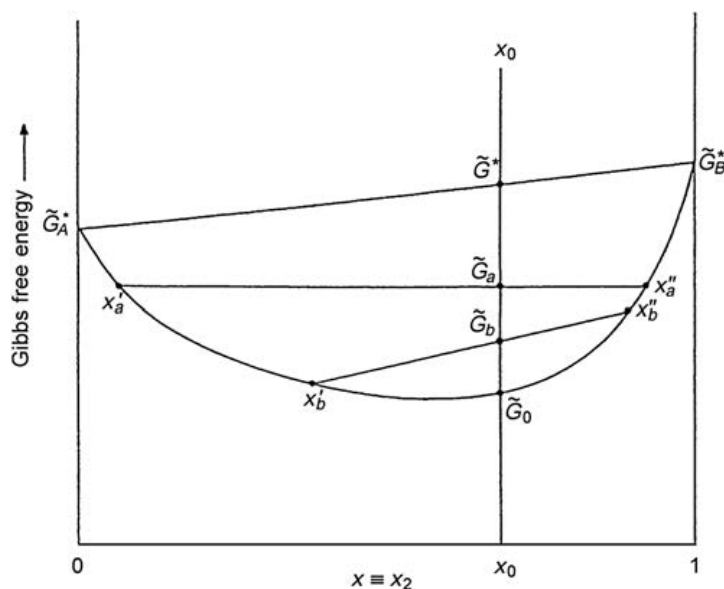


FIGURE 3.8.5

Schematic representations of the change in Gibbs free energy with composition for a binary homogeneous liquid solution.

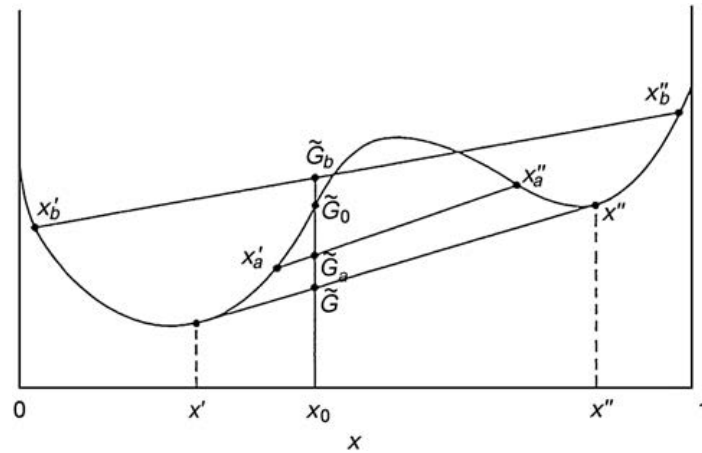


FIGURE 3.8.6

Schematic representations of the change in Gibbs free energy with composition for a binary heterogeneous liquid solution. A single phase is stable for $0 \leq x \leq x'$ and $x'' \leq x \leq 1$; a biphasic mixture is encountered in the intermediate composition range.

By contrast, consider the free energy curve as a function of composition as sketched in Figure 3.8.6, which reproduces curve \tilde{G} in Figure 3.8.4(c). If an alloy of composition x_0 between the two minima were to exist as a homogeneous solution, its free energy would be given by the point \tilde{G}_0 which falls on the curve. On the other hand, if the alloy were a heterogeneous mixture of composition x'_a and x''_a for component 2, the free energy of the system would be lowered to \tilde{G}_a . By choosing x' and x'' to be more widely separated in composition one progressively lowers the free energy until a minimal value G is reached when the two phases are of composition x' and x'' ; here the straight line connecting these particular mole fraction values forms a tangent to the two curves near the local minima. Any attempt to spread the composition of the two phases further will lead to a rise in free energy, as is illustrated for x'_b and x''_b , with a corresponding value for \tilde{G}_b .

The stable state of the system under study may thus result in a heterogeneous mixture of composition x' and x'' . In fact, in the range $x' < x < x''$, the alloy or solution consists of two phases of composition x' and x'' in the proportions $(x - x')/(x'' - x')$ and $(x'' - x)/(x'' - x')$ are given by the Lever Rule. Note that the proportions change linearly with composition x . However, in the ranges $x < x'$ or $x > x''$, the homogeneous solution is stable, as is seen by inspection of Figure 3.8.6.

The tangency effect described above has a physical interpretation: it specifies the slope of the free-energy curve \tilde{G} vs x at the points of tangency x' and x'' ; in other words, it is the chemical potential of the solution at the two compositions x' and x'' . The two chemical potentials are obviously identical, which is the requirement that must prevail at equilibrium.

Distribution of a Solution Among Two Phases

The changeover of the A–B alloy system from an A-rich to a B-rich homogeneous phase with composition at fixed temperature is more easily visualized with the aid of Figure 3.8.7, in which we represent the fraction f of the total mole numbers in phase ' and phase '. As pure B is added to pure A, the B atoms form a homogeneous solution in A up to the composition x' at which the solution is saturated with B. Any further addition of B results in the formation of a second phase for which $x = x''$, in which units of type A are considered dissolved in B. With further addition of B, the proportion of the

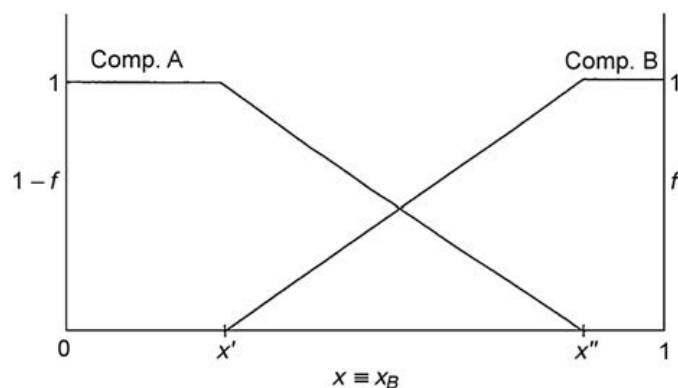


FIGURE 3.8.7

Variation of the makeup of a binary system with relative composition (e.g., mole fraction), shown as a plot of $1 - f$ and of f vs x .

second phase at fixed composition x'' increases at the expense of the first until the phase boundary at $x = x''$ is reached. For $x > x''$ only the homogeneous solution of B containing progressively less A is stable. In the heterogeneous region, the compositions of the two phases of the mechanical mixture remain constant, but the relative total amounts of material in each phase changes with alterations in x .

Generalization to Several Components

The presentation may readily be generalized to a system in which more than two phases appear. A typical example is shown in Figure 3.8.8; here the homogeneous and heterogeneous composition ranges are delineated by use of an imaginary string that is tightly wound around the curves between

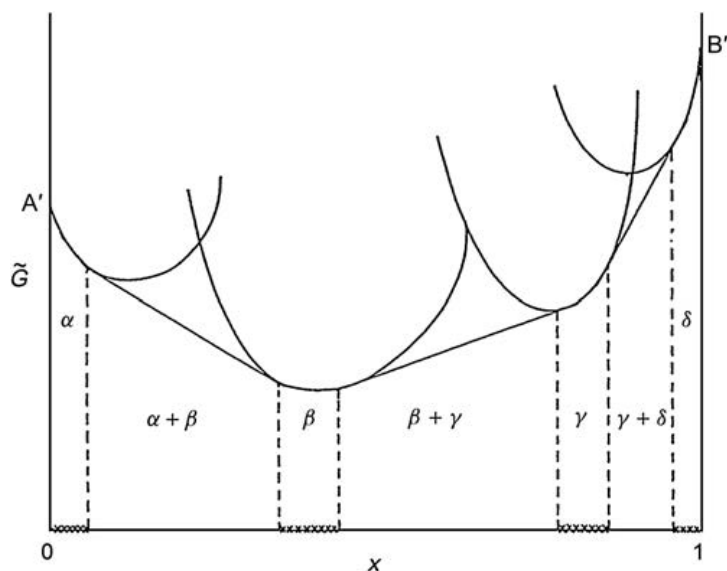


FIGURE 3.8.8

Gibbs free energy as a function of mole fraction x with several homogeneous phases of different composition are formed. Stable single phases are indicated by cross-hatching on the x scale.

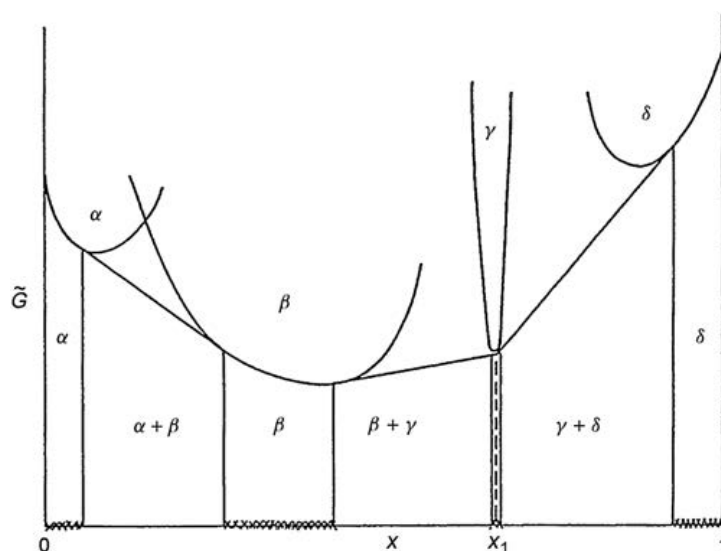


FIGURE 3.8.9

Gibbs free energy as a function of mole fraction x when several homogeneous phases of different composition are formed, one of which is a compound of composition $A_{1-x_1} B_{x_1}$. Stable single phases are indicated by cross-hatching on the x scale.

points A' and B' in the diagram to exhibit all possible *common tangent constructions*. It is customary to designate phases consecutively by Greek lowercase letters in alphabetical order. The various phases and their composition ranges are indicated on the diagram.

In general, if $\Delta\tilde{H}$ is small, as is likely to be the case for homogeneous solutions, the free energy, plotted as a function of composition, forms a broad, shallow U-shaped curve, and the ranges of composition over which the single phases are stable are large. The straight sloping lines delineate compositional ranges that are heterogeneous. By contrast, when a compound is formed, deviations from the appropriate stoichiometric ratio remain very small. This is reflected in the extremely sharp rise of the free energy as the composition is changed even very slightly from the appropriate stoichiometric ratio. A situation of this type is depicted in Figure 3.8.9; it is seen that the composition of the γ phase is stable over only a narrow range. The composition of the compound does not necessarily coincide with an ideal stoichiometric value; for example, the compound CuAl_2 does not exist, but a compound on the Al-rich side of this value is stable.

Construction of Several Types of Phase Diagrams

We are now ready to construct and interpret the commonly encountered phase diagrams, based on the preceding discussion. The mystery that often surrounds the interpretation of phase diagrams may be dispelled by relating the latter to the shape of the free energy curves for liquid, solids, or gases. We follow the exposition by A. Cottrell.⁷ Let us start with the simple case where the liquid solution is homogeneous throughout the entire composition range; the corresponding free energy curves are then U shaped, as depicted in Figure 3.8.5. In our first example, Figure 3.8.10, the solid state also exists only as a homogeneous solution. High temperatures favor the disordered state, so that the free energy of the

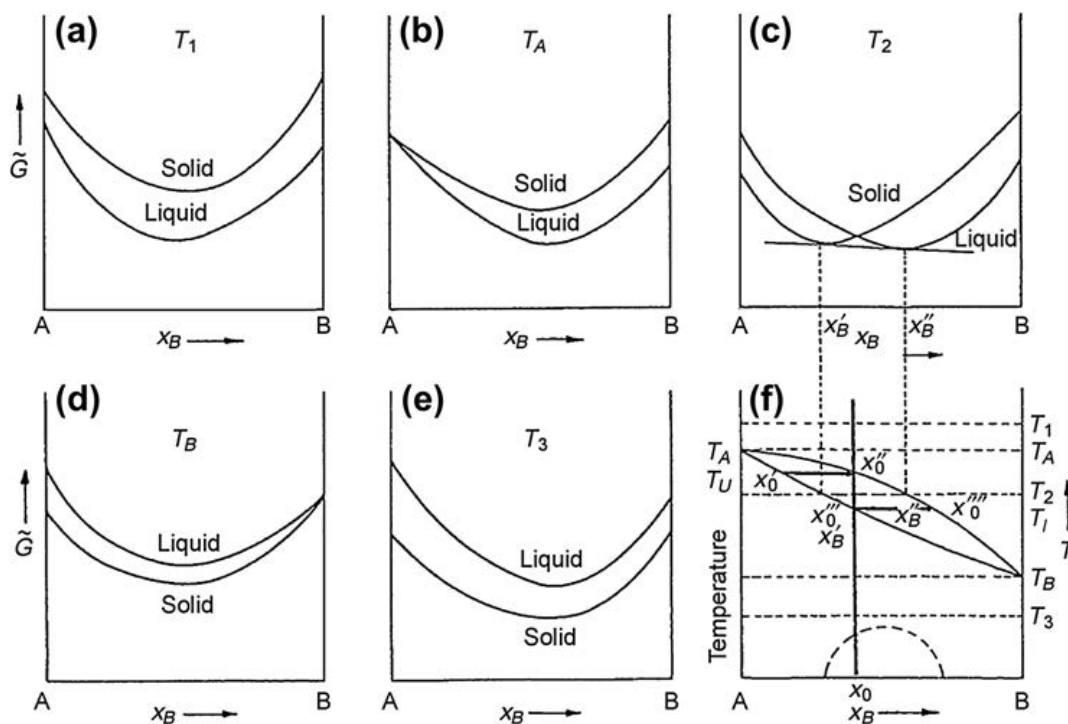


FIGURE 3.8.10

Correlation of a standard phase diagram with the temperature change of free-energy curves of simple liquid and solid phases.

solid lies above that of the liquid phase. Quite generally, as the temperature is lowered, the free-energy curve of the solid moves past that of the liquid [why?, see Exercise 3.8.13], and the shape of each curve (i.e., the skewness of the U shapes) will also be altered. Thus, with diminishing temperature, the two free-energy curves will ultimately intersect, so that a common tangent construction is called for that indicates the presence of biphasic mixtures. In Figure 3.8.10(a), the temperature T_1 is sufficiently high that the entire free-energy curve for the liquid, $G_l(x)$ lies below that for the solid, $G_s(x)$; the liquid state is stable over the entire composition range x . As the temperature is lowered to a value T_A (part (b)), the two free-energy curves touch at the composition $x = 0$; solid and liquid now coexist for the pure phase, so that T_A represents the melting point of pure A. However, for $x > 0$ the free energy of the liquid remains below that of the solid; the solution remains in the liquid state. As T is reduced further to the value T_2 (part (c)), the $G_l(x)$ and $G_s(x)$ curves intersect, such that in the composition regions $0 \leq x < x'_B$ or $x''_B < x \leq 1$ a single homogeneous solid or homogeneous liquid phase respectively is stable; in the intermediate range, the common tangent construction shows that the system divides into a phase mixture involving a solid of composition x'_B in equilibrium with a liquid of composition x''_B . With a further decrease in temperature to the value T_B (part (d)), the curves G_l and G_s touch at $x_B = 1$; this is the melting point of pure B. For $T < T_B$ (part (e)), $G_s < G_l$ for all x ; the homogeneous solid phase is now the stable one over the entire composition range.

The preceding information may be assembled into the equilibrium phase diagram shown in part (f), which is typical for this type of system. The diagram shows the T - x regions over which either the

homogeneous solid (below the lower curve) or liquid (above the upper curve) is stable; the two corresponding boundary lines are known as the *solidus* and *liquidus*. The lens-shaped T - x region between these represents an unstable or forbidden range called a *miscibility gap*; no mixtures are stable in this region of the phase diagram. A *tie-line* connects the solid of composition x'_B with the liquid of different composition x''_B with which it is in equilibrium. The lens-shaped “forbidden” region thus traces out the range of the tangent construction at each relevant temperature.

The vertical line indicates what happens as the temperature of the system of fixed composition x_0 is lowered. Initially the liquid phase is stable down to temperature T_U where x_0 intersects with the liquidus curve. At this stage, the system separates into two phases of composition x'_0 and x''_0 in amounts such that the average x_0 composition is maintained. On further cooling, the x' values continually shift to the right along the lower curve, and the x'' values (connected to x' via a tie line) similarly shift to the right along the upper curve. Their relative amounts change as well, according to the lever rule, so as always to maintain the same average composition x_0 . This shift continues until one reaches the temperature T_L at which mole fraction x'_0 for component A is in equilibrium with B at mole fraction x''_0 . On further cooling, a solid solution of uniform composition x_0 is maintained that remains stable down to the point where another phase separation, indicated by the dome-shaped dotted curve, may be encountered. The Ag–Au, Cu–Ni, Au–Pt, and U–Zr alloys are representative examples of such systems.

Variants of this scheme are encountered for alloys where $G_s(x)$ has a significantly smaller curvature than $G_l(x)$. As shown in Figure 3.8.11, with diminishing temperature $G_s(x)$ moves past $G_l(x)$; in this process, there are at first one and then two intersections between the two curves. These call for the

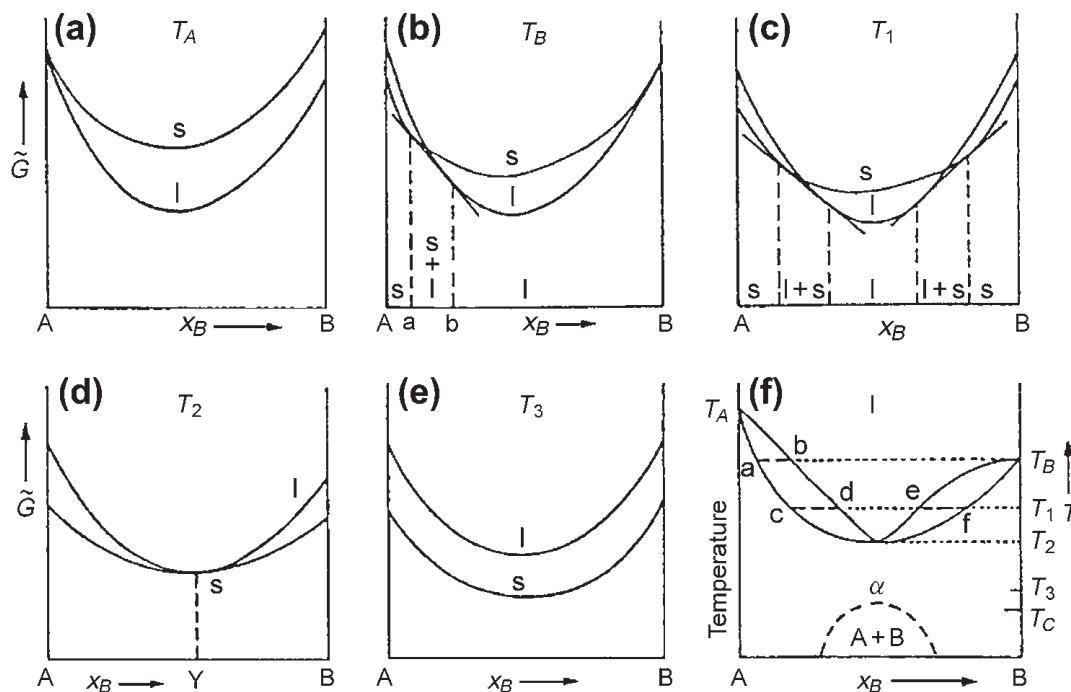


FIGURE 3.8.11

Correlation of a phase diagram developing a minimum with the temperature change of free-energy curves of liquid and solid phases.

usual common tangent construction. With diminishing T these regions move inward until they meet at a common point. The relationship between the free-energy curves and the phase diagram on the right should be clear; again, the regions between areas a and b in part (b), or between c and d, or between e and f in part (c) represent miscibility gaps. These lens-shaped regions represent “forbidden” zones in the sense described above—no homogeneous single phase exists under the conditions covered in those particular T - x ranges. Figure 3.8.11(f) may be viewed as two back-to-back phase diagrams of the type shown in Figure 3.8.10(f), and can thus be interpreted in a similar manner. The inverse situation is depicted in Figure 3.8.12; it arises when the curvature of $G_s(x)$ significantly exceeds that of $G_l(x)$.

In the above two cases, the solidus and liquidus curves meet tangentially to an isothermal line at a congruent point; the solution freezes at this temperature without any change in composition. Au–Ni alloys exhibit the behavior depicted in Figure 3.8.11. The melting point of the intermediate composition is below that of either pure material. Inasmuch as $\Delta\tilde{H}_c > 0$ for this case, the solid solution for $T < T_c$ is less stable than a mixture of phases; this is indicated by the dotted curve at the bottom of the diagram.

A second case frequently encountered involves a solid whose components are only partially miscible and in which no intermediate phases are formed. The solid free-energy curve exhibits a maximum flanked by two minima at intermediate compositions, and the liquid free-energy curve is U shaped. The relevant free energy curves are shown in Figure 3.8.13. At temperature

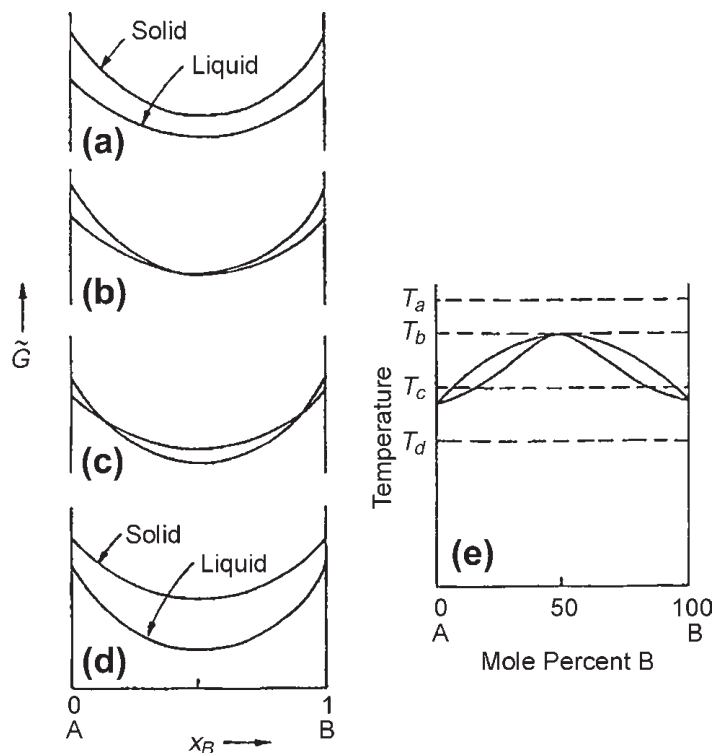


FIGURE 3.8.12

Correlation of a phase diagram developing a maximum with the temperature change of free-energy curves of liquid and solid phases.

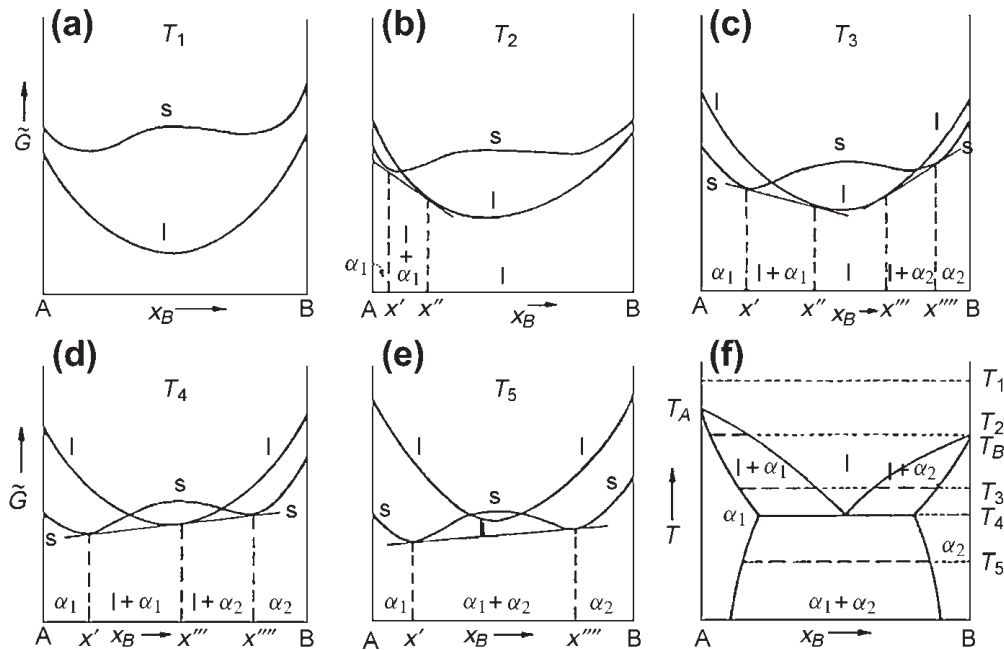


FIGURE 3.8.13

Derivation of phase diagram from the temperature change of free-energy curves of liquid and solid stages are only partially miscible.

$T = T_1$, $G_l(x) < G_s(x)$ for all x ; the homogeneous liquid phase is stable over the entire composition range. At a particular value $T = T_2$, somewhat below the melting point of pure A, the free-energy curves for solid and liquid intersect, as shown in part (b). By the common tangent construction, we see that for $0 \leq x \leq x'$, the homogeneous solid alloy is stable; for $x' \leq x \leq x''$ solid of composition x' is in equilibrium with liquid of composition x'' ; for $x > x''$, the homogeneous liquid phase is stable. Part (c) is typical of a temperature T_3 at which G_s and G_l intersect both at the A-rich and at the B-rich ends of the diagram. Here, homogeneous solid solutions exist for the composition ranges $0 \leq x \leq x'$ and $x'''' \leq x \leq 1$; solid of composition x' is in equilibrium with liquid of composition x'' , and liquid of composition x'''' is in equilibrium with solid of composition x'''' ; in the range $x'' \leq x \leq x''''$, the homogeneous liquid phase is stable. Further cooling narrows the homogeneous x'' – x'''' range until it vanishes at temperature T_4 where $x'' = x''''$. This point, known as the eutectic temperature, is the lowest temperature at which an alloy still remains liquid. This liquid of composition x'''' is in equilibrium with two solid phases of composition x' and x'''' . The eutectic solid is a heterogeneous mixture of two solid phases of composition x' , x'''' . For $T = T_5 < T_4$, only the solid is stable, but in the composition range $x' < x < x''''$ of part (e) one encounters a heterogeneous mixture of two phases of composition x' and x'''' in mutual equilibrium. The corresponding phase diagram is shown in part (f). Ag–Cu, Pb–Sn, Pb–Sb, Al–Si, and Cr–Ni are examples of systems exhibiting those properties which arise when the end members crystallize in the same structure. The ℓ region in Figure 3.8.13(f) covers the T – x range of the homogeneous liquid phase; α_1 and α_2 cover conditions under which homogeneous solid A-rich or B-rich alloy phases are stable. The remaining parts of the diagram involve “forbidden,” two-phase zones.

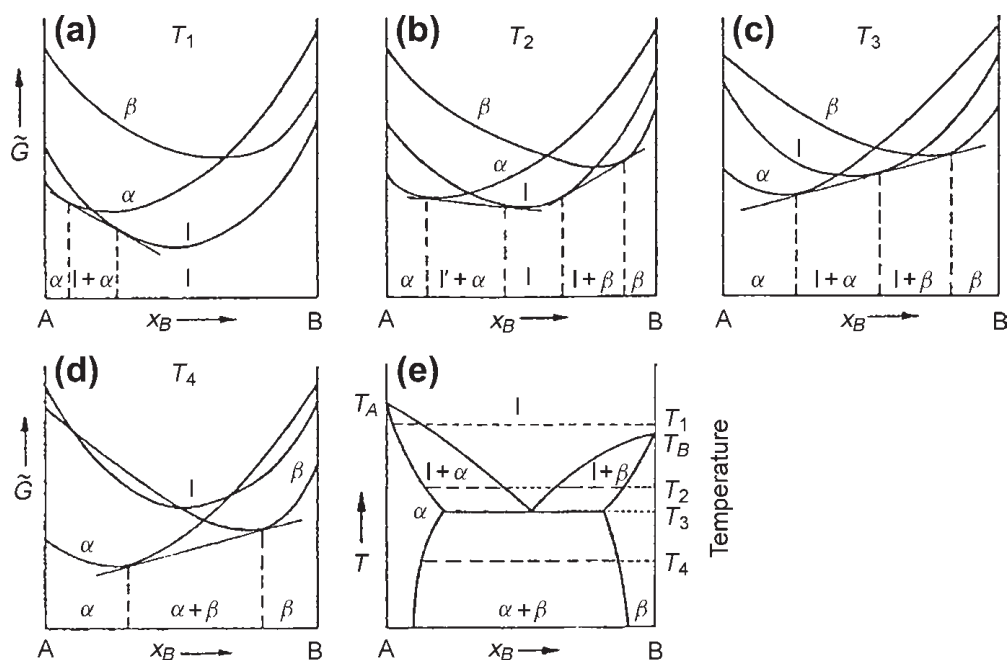


FIGURE 3.8.14

Derivation of a phase diagram from the temperature change of free-energy curves of a liquid and two solid phases.

One also encounters a similar system for two materials A and B which crystallize in different habits; the construction of the corresponding phase diagram is indicated in Figure 3.8.14. This is handled by invoking two free-energy curves, α and β for the two different solid phases. Their intersections with G_l at various temperatures are similar to those of the preceding diagram.

By now you will be able to construct and interpret the phase diagram in Figure 3.8.15 on a similar basis. This situation arises mainly when the melting points of pure A and B differ considerably and the solid phase is inhomogeneous, so that the “hump” changes dramatically with T . Diagrams of this type are classified as belonging to the *peritectic* type; the temperature T_P is the *peritectic temperature*; above it no solid α_2 phase is formed for any composition; below it there is a wide composition range over which the homogeneous solid α_2 alloy system is stable. The $l + \alpha_1$, $l + \alpha_2$, and $\alpha_1 + \alpha_2$ regions of the phase diagram show T - x ranges over which biphasic mixtures are encountered. The remaining regions indicate where monophasic solid or liquid solutions are to be found.

We next turn to more complex cases involving formation of intermediate compounds. In Figure 3.8.16, the relative positions of the free energy curves for α , β , and γ , and of liquid phase are such that an initial intersection of the G_l curve occurs with the G_s curve for phase β , as shown in part (b). On further cooling, more intersections arise as shown in parts (c) and (d); this leads to the subsequent appearance of the α and γ components. At still lower temperatures, two eutectics are formed, first one between β and α and then, a second between β and γ . Finally, for, $T = T_5$ one obtains three

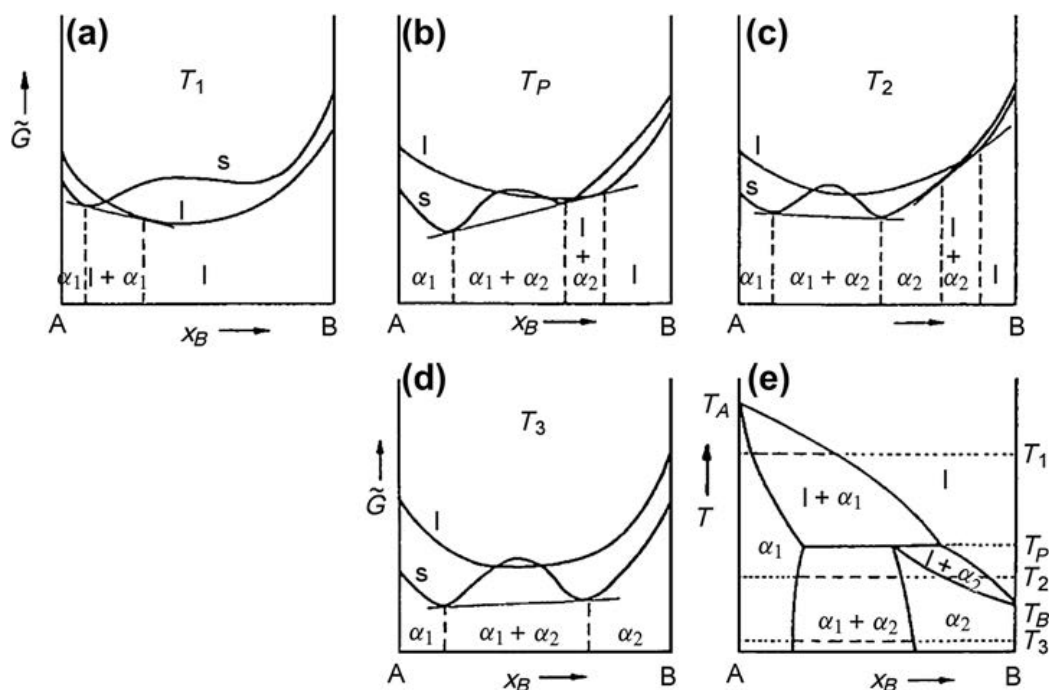


FIGURE 3.8.15

Derivation of phase diagram from the temperature change of free-energy curves of a miscible liquid and two partially miscible solid phases. The melting points of A and B are widely different.

homogeneous alloys phases in three composition ranges near $x = 0(\alpha)$, $x \approx 1/3(\beta)$ and $x = 1(\gamma)$, as well as two-phase regions in the intermediate composition ranges. You should carefully check how the phase diagram of Figure 3.8.16(f) is assembled from an examination of parts (b)–(e). Example 3.8.5 calls for the generation of free energy curves whose gradual intersection leads to a peritectic diagram of the type illustrated in Figure 3.8.17. Phase diagrams of this type are quite common; they tend to arise when the melting points of the pure components are very different. You should carefully distinguish between the many different regions over which monophasic and biphasic regions are stable.

A general feature of the phase diagrams explored in Figures 3.8.16 and 3.8.17 is the existence of a maximum, corresponding to the composition of the intermediate β phase. This reflects the composition at which G_l and G_s first become tangent to each other. However, this point generally does not coincide exactly with the minimum in the free energy curve for the solid β phase; the composition of the intermediate phase then does not agree precisely with the ideal stoichiometric formula for the phase.

Finally, we direct attention to Figure 3.8.18, for a study on how the diagram of part (f) arises. More complex types of phase diagrams will not be explored here, but the general methodology should be clear from the preceding examples.

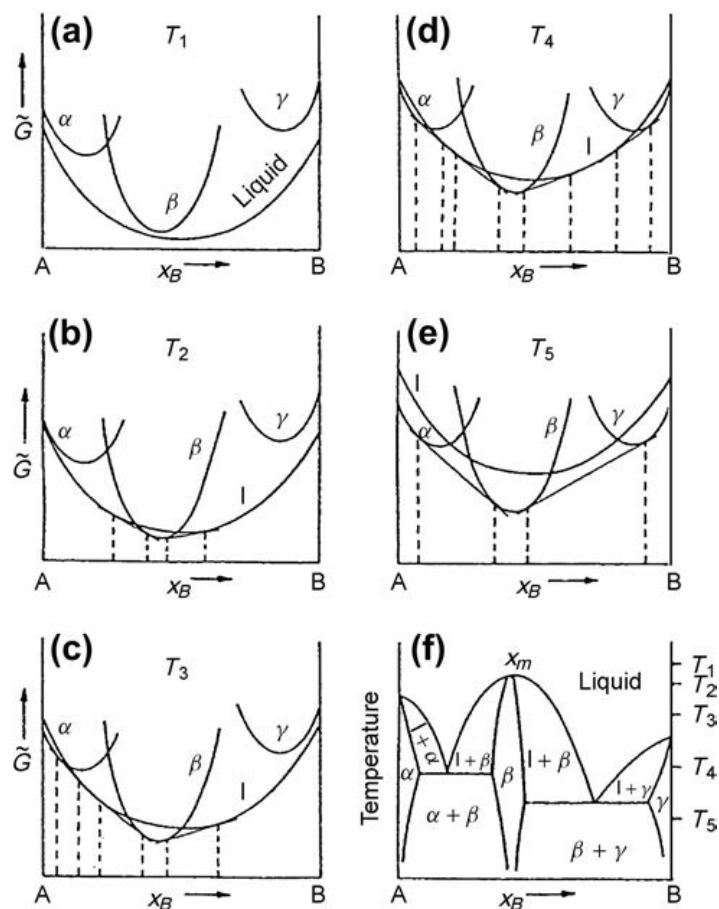


FIGURE 3.8.16

Derivation of a phase diagram from the temperature change of free-energy curves of a miscible liquid and three solid phases.

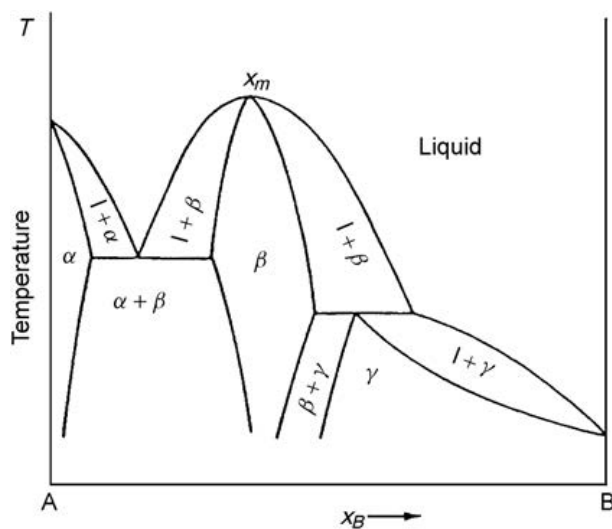


FIGURE 3.8.17

A compound peritectic phase diagram.

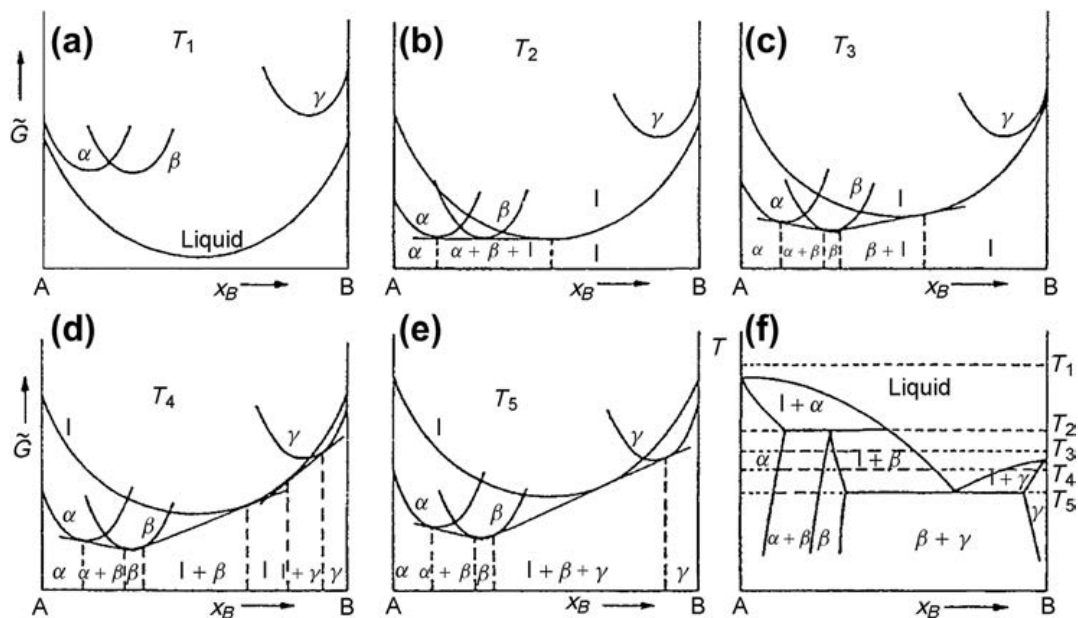


FIGURE 3.8.18

Derivation of a complex phase diagram from the temperature change of free-energy curves of a miscible liquid and three solid phases.

Exercises

- 3.8.7.** A. Cottrell, *Theoretical Structural Metallurgy*, 2nd Ed. (Arnold, London, 1955).
- 3.8.8.** Examine Figure 3.8.19(a) and answer the following questions: (a) Identify the areas labeled 1–6. (b) Describe and interpret the events occurring at temperatures T_A , T_B , T_C . (c) Describe the events taking place when alloys of compositions L, M, and N are cooled from $T > T_A$ to $T > T_D$.
- 3.8.9.** Label all the areas of the peritectic diagram of Figure 3.8.19(b). State what happens as liquids of composition a, b, c, d, and e are cooled from temperature T_1 to temperature T_2 .
- 3.8.10.** On phase diagram 3.8.19(c), identify the regions 1–5. Can such a phase diagram arise if the solid free energy curve is U-shaped and the liquid free-energy curve displays a maximum at intermediate compositions?
- 3.8.11.** Identify the regions 1–11 of the phase diagram, Figure 3.8.19(d). What feature in the free-energy curves gives rise to the very narrow line running vertically at composition $x = 1/2$?
- 3.8.12.** Construct a set of free-energy curves that lead to the formation of the compound peritectic phase diagram depicted in Figure 3.8.17.
- 3.8.13.** On the basis of Eqs. (3.8.2)–(3.8.4) provide a rationale why the free energy of a solid phase tends to shift more rapidly with temperature than that of a liquid phase.
- 3.8.14.** If really brave, construct a phase diagram for the case where both solid and liquid free-energy curves exhibit maxima flanked by two minima.

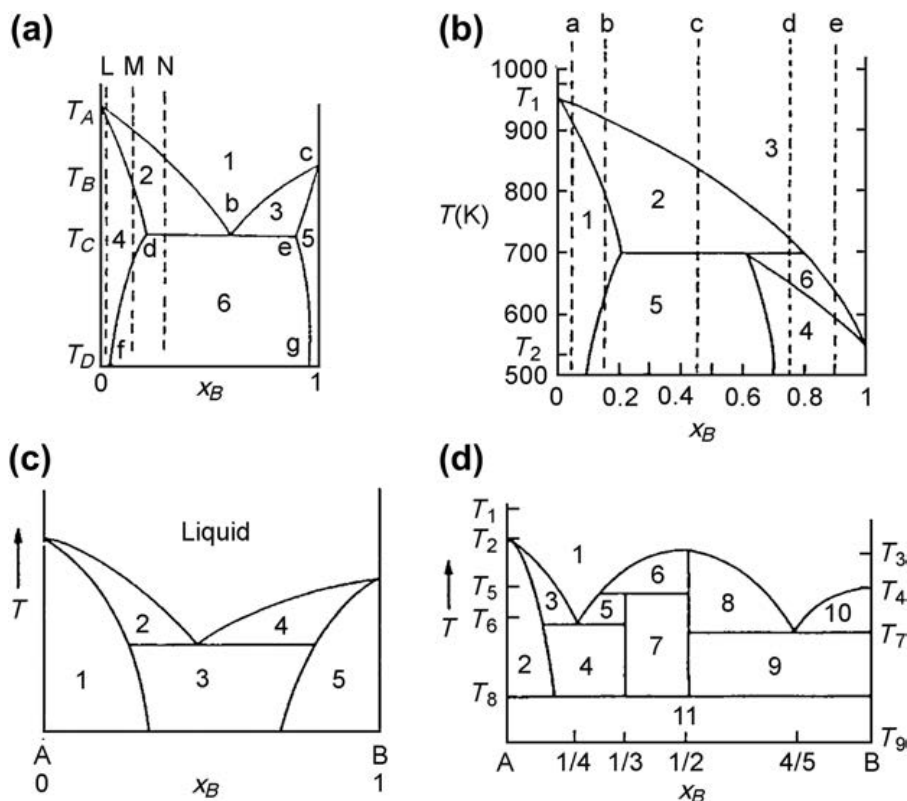


FIGURE 3.8.19

Phase diagrams to be rationalized in terms of the questions posted in Exercises 3.8.8–3.8.11.

3.9 Dependence of Higher Order Phase Transitions on Temperature

We investigate here the course of a higher order phase transition as the temperature of the system is raised. The first-order transitions had been treated in Section 2.3. On general principles, it is anticipated that rising temperatures broaden the homogeneity range of an inhomogeneous system. For, at higher T the negative entropic contribution to the free energy, $-T\Delta\tilde{S}_m$, begins to compete with and ultimately outweigh the positive enthalpic contribution, $\Delta\tilde{H}_m$, which was primarily responsible for the initial phase separation. We seek to establish the temperature dependence of the homogeneity range of the solution.

The Bragg–Williams Approximation

Consider first the symmetric case of the preceding section, in which the Gibbs free energy remains unaltered under an interchange of the indices 1 and 2 of the binary mixture. This represents the so called Bragg–Williams approximation.

On setting $x_2 \equiv x$ and $x_1 = 1 - x$, Eq. (3.8.17) assumes the form

$$\Delta\tilde{G}_m \equiv \left(\tilde{G}_m - \tilde{G}^* \right) / RT = (1-x)\ln(1-x) + x\ln x + (w/RT)x(1-x). \quad (3.9.1)$$

Plots of $(\Delta\tilde{G}_m/RT)$ vs x for several values for the dimensionless parameter RT/w are exhibited in Figure 3.9.1. Close inspection reveals that either at very low temperatures, or for very large positive w , the last term outweighs the entropy term, except near the end points where $x \rightarrow 0$ or $x \rightarrow 1$. Correspondingly, the major portions of the top curves in Figure 3.9.1 are positive, but two minima are symmetrically encountered in the negative portions of the curve. For $RT/w > 0.37$, the curve lies entirely in the negative domain, and for $RT/w > 1/2$, it no longer exhibits local minima. In the latter case $\partial^2\Delta\tilde{G}_m/\partial x^2 > 0$ for all x , so that the mixture remains homogeneous over the entire composition range above the critical value of $(RT/w)_c = 1/2$.

The net effect is to bring the local minima, shown in Figure 3.9.1, together with rising T until they merge for $x = 1/2$ at the critical temperature. The effect is shown as a dashed curve in the figure. We wish to quantify the temperature dependence of the homogeneity range of a binary solution on the basis of this simple model.

The locus of the minima, shown as the dashed curve, is constructed by reading off the locations in the minima in the free energy curves from each of the plots generated from Eq. (3.9.1). This leads to a plot of RT/w vs x , shown in Figure 3.9.2 and which, at constant w , traces the immiscibility range with temperature. For compositions within the dome-shaped curve, the binary solution is unstable. As T is lowered, the two phases approach the pure limiting compositions $x = 0$ and $x = 1$, if the system could be equilibrated. Above the critical value $RT/w = x = 1/2$, the solution is monophasic over the whole composition range.

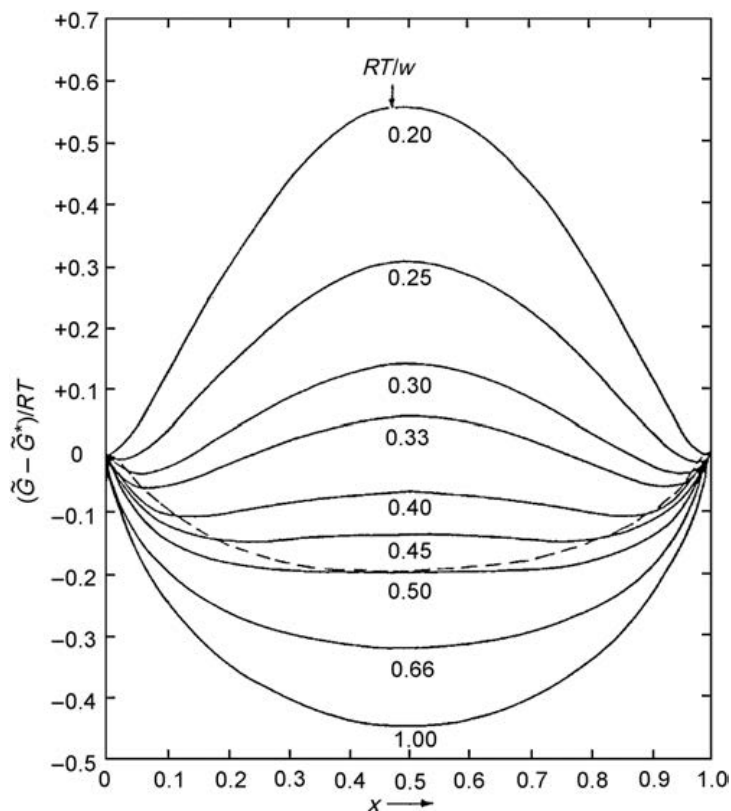


FIGURE 3.9.1

Variation of reduced molar Gibbs free energy of mixing with composition for a mixture with $w > 0$. Different curves correspond to different RT/w values. Dashed curve shows the locus of points for local minima.

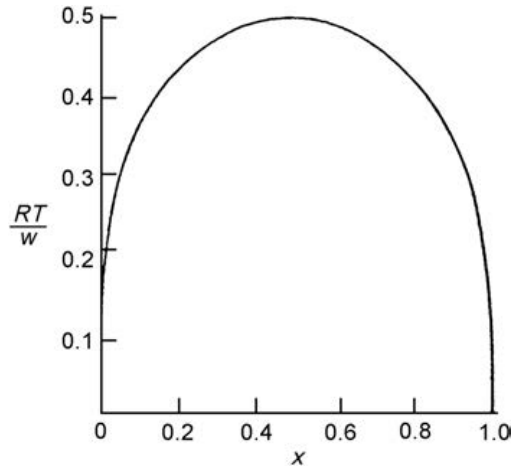


FIGURE 3.9.2

Separation of phases for a binary mixture. Region outside curve represents domain of heterogeneous phases.

Variation of the Gibbs Free Energy with Temperature in the Bragg–Williams Approximation

In the above model, for temperatures $RT/w < 1/2$, the splitting of the solution into two phases of composition x' and x'' requires the specification of the relative amounts of material in each phase, as already explained in Section 3.8. For ease of reference, we repeat the argument: the mole numbers for component 2 are given by $n_2 = n'_2 + n''_2$, or $n_2/n = (n'_2/n')(n'/n) + (n''_2/n'')(n''/n)$. Let $f \equiv n''/n$. Let $f \equiv n''/n$ represents the fraction of material associated with the '' phase. On converting to mole fractions, we then introduce the conservation law for component 2 as ($x_2 \equiv x$),

$$x = x'(1 - f) + x''f, \quad (3.9.2)$$

which may be solved for

$$f = \frac{x - x'}{x'' - x'}, \quad (3.9.3)$$

in which x is the mole fraction of component 2 in the *homogeneous* phase. Equation (3.9.3) is known as the *lever rule*.

In using Eq. (3.9.3), one must remember that x' or x'' are no longer variables under the control of the experimenter; rather, they are uniquely determined by the solution temperature. In studying this effect, it is important to keep track of quite a few quantities that are listed in Table 3.8.I for easy reference.

For a two-phase heterogeneous mixture of constituents A and B, we write

$$G = G' + G'', \quad (3.9.4)$$

in which G' and G'' are the Gibbs free energies for the two phases of composition x'_B and x''_B . Then, for the ' phase we set

$$G' = n'_A \tilde{G}_A^* + n'_B \tilde{G}_B^* + RT \{ n'_A \ln n'_A + n'_B \ln n'_B \} + w(T) (n'_A n'_B / n), \quad (3.9.5)$$

with a corresponding expression for G'' .

Referring to lines 2 and 8 of Table 3.9.I, and introducing the definition of $n\tilde{G} = G$ on the left of Eq. (3.9.5), we find

$$n'\tilde{G}' = n'_A\tilde{G}_A^* + n'_B\tilde{G}_B^* + RTn'\left\{(1-x')\ln x' + x'\ln x'\right\} + w(T)n'x'(1-x'). \quad (3.9.6a)$$

$$n''\tilde{G}'' = n''_A\tilde{G}_A^* + n''_B\tilde{G}_B^* + RTn''\left\{(1-x'')\ln x'' + x''\ln x''\right\} + w(T)n''x''(1-x''). \quad (3.9.6b)$$

Here we have assumed that $w(T)$ is the same function for both phases. This possibly poor approximation keeps the subsequent operations manageable. (You are invited to explore the complications that arise when different w values are assigned to the two phases; more on that topic below.) Accordingly, the total free energy reads $G = n'\tilde{G}' + n''\tilde{G}'' = n\tilde{G}$, so that by lines 6 and 8 of Table 3.9.I:

$$\begin{aligned} \tilde{G} &= (n''/n)\tilde{G}' + (n'/n)\tilde{G}'' \\ &= (1-f)\tilde{G}_A^* + f\tilde{G}_B^* + RT(1-f)\left\{(1-x')\ln(1-x') + x'\ln x'\right\} + RTf\left\{(1-x'')\ln(1-x'') \right. \\ &\quad \left. + x''\ln x''\right\} + w(T)\left\{(1-f)x'(1-x') + fx''(1-x'')\right\}. \end{aligned} \quad (3.9.7)$$

Within the present approximations, the minima in Figure 3.9.1 are symmetrically displaced with respect to $x = 0$ and $x = 1$, whence $x' = 1 - x''$ and $1 - x' = x''$. Equation (3.9.5) then reduces to ($\tilde{G}^* \equiv x_A\tilde{G}_A^* + x_B\tilde{G}_B^*$)

$$\tilde{G}/RT = \tilde{G}^*/RT + \left\{(1-x'')\ln(1-x'') + x''\ln x''\right\} + (w(T)/RT)x''(1-x''). \quad (3.9.8)$$

The preceding equation, somewhat fortuitously, has precisely the same form as Eq. (3.9.1); however, it differs radically from the earlier version: $x''(T)$ is not arbitrarily adjustable but rather is specified by locating the minima of Eq. (3.9.1) when $RT/w < 1/2$. Thus, Eq. (3.9.8) depends solely on T in contrast to Eq. (3.9.1), where the composition variable x is under the direct control of the experimenter.

To show how \tilde{G} now varies with temperature, one must determine the temperature dependence of x'' by minimization of Eq. (3.9.8), as shown in conjunction with Eq. (3.8.13), with $B \equiv w/R$. This requires a numerical solution of the transcendental Eq. (3.8.14). This variation is not of particularly great interest. Instead, it is of greater relevance to study how the enthalpy changes with temperature. Proceeding as usual, the enthalpy reads $H = -T^2[\partial(G/T)/\partial T]$, in which, for $RT/w < 1/2$, $x'' = x''(T)$ is an implicit function of temperature. Accordingly, the differentiation process yields

$$-\frac{\tilde{H}}{RT^2} = -\frac{\tilde{H}^*}{RT^2} + \left\{\ln \frac{x''}{1-x''} + \frac{w(T)}{RT}(1-2x'')\right\} \frac{dx''}{dT} + x''(1-x'')\left[\frac{1}{RT}\frac{dw(T)}{dT} - \frac{w(T)}{RT^2}\right]. \quad (3.9.9a)$$

On account of Eq. (3.8.14), the central term in braces drops out; Eq. (3.9.9a) may then be rearranged to read

$$\tilde{H} = x_A\tilde{H}_A^* + x_B\tilde{H}_B^* + \left(w(T) - T\frac{dw(T)}{dT}\right)x''(1-x''). \quad (3.9.9b)$$

It is conventional at this point to introduce a quantity termed the *degree of order*, or *order parameter*, s_p , defined by

$$s_p \equiv 2x'' - 1 \text{ or } x'' = (1/2)(1 + s_p); \quad (-1 \leq s_p \leq 1), \quad (3.9.10)$$

with which the equilibrium condition Eq. (3.8.14) assumes the simpler form

$$\ln[(1 + s_p)/(1 - s_p)] = (w/RT)s_p. \quad (3.9.11)$$

Order parameters are routinely encountered in the treatment of phenomena dealing with phase changes or critical phenomena, and will be discussed further in Section 7.5. Here we develop a somewhat specialized approach.

Equations (3.9.8) and (3.9.9) now read,

$$\Delta\tilde{G}_m = RT \left\{ (1/2)(1 + s_p) \ln(1 + s_p) + (1/2)(1 - s_p) \ln(1 - s_p) - \ln 2 + (w/4RT) \right\} (1 - s_p^2), \quad (3.9.12)$$

and

$$\Delta\tilde{H}_m = \left(w(T) - T \frac{dw(T)}{dT} \right) \frac{1}{4} (1 - s_p^2). \quad (3.9.13)$$

Equation (3.9.11) is frequently written out in the equivalent form

$$\tanh(w s_p / 2RT) = s_p, \quad (3.9.14)$$

and one conventionally defines a *characteristic temperature* T_λ by $T_\lambda \equiv w/2R$ usually coupled to the assumption that w is constant. Equation (3.9.14) then reads

$$T_\lambda / T = (\tanh^{-1} s_p) / s_p. \quad (3.9.15)$$

Variation of Enthalpy with Temperature

The numerical solution of Eq. (3.9.15) yields the dependence of the order parameter; the resulting universal functional relationship is shown in Figure 3.9.3. s_p changes little in the range $0 \leq T/T_\lambda \leq 0.3$, where $x'' \approx 1$. With an increase in T/T_λ , there is a gradually accelerating dropoff in s_p , until for $T/T_\lambda \rightarrow 1$ s_p drops abruptly to zero, corresponding to $x'' = 1/2$. Thus, s monitors the gradual changeover from a complete phase separation ($s = 1$) at $RT/w = 0$ to an intimate mixture of the two components ($s = 0$) at $RT/w \approx 0.49$.

Using the $s_p(T)$ relation shown in Figure 3.9.3, one can determine $\Delta\tilde{H}_m$ via Eq. (3.9.13). The result is shown in Figure 3.9.4 as a plot of $\Delta\tilde{H}_m / (1/4)w$ vs T/T_λ , on neglect of the term $dw(T)/dT$. At first, $\Delta\tilde{H}_m$ is close to zero, but as T/T_λ increases beyond 0.3 the enthalpy of mixing increases rapidly to its final value of $(1/4)w$ at $T = T_\lambda$.

The heat capacity at constant pressure is now found through the relation $\Delta\tilde{C}_m|_p = (\partial\Delta\tilde{H}_m/\partial T)_m$. In Figure 3.9.5, with $w = 2R$, we show the resulting plot of $\Delta\tilde{C}_m|_p/R$ vs T/T_λ derived from the slope in Figure 3.9.4. As the temperature rises, the heat capacity at first remains close to zero. Beyond $T/T_\lambda \approx 1/3$, the heat capacity increases nearly linearly, with a sharp drop off back to zero at $T = T_\lambda$.

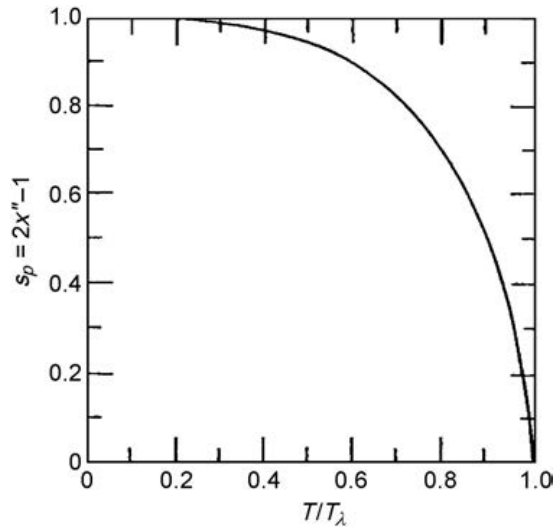


FIGURE 3.9.3

Variation of order parameter s_p with T/T_λ as given by Eq. (3.9.15); $T_\lambda \equiv w/2R$.

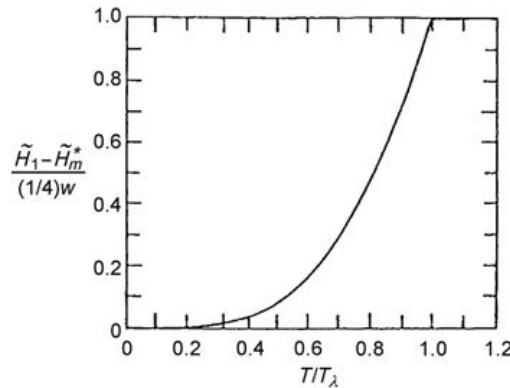


FIGURE 3.9.4

Change of reduced enthalpy of mixing with reduced temperatures, as given by Eq. (3.9.13) with $dw/dT = 0$.

This figure has approximately the shape of the Greek capital letter Λ and hence is frequently called a *lambda anomaly*: T_λ is known as the *lambda point*. Figure 3.9.5 once more illustrates that the transition from the biphasic to the monophasic regime takes place over a considerable range of temperature. This gradual transformation is known as a *higher order transition* that contrasts sharply with first-order phase transformations discussed in Section 2.3. As the temperature is raised, continually greater amounts of energy are required to achieve a further rise in T while the system moves close to the region of homogeneous stability, the onset of which abruptly halts the heat capacity anomaly.

Physical Interpretation

We briefly consider the physical interpretation in which the order parameter plays a central role. At $T = 0$, $s_p = 1$ so that $x'' = 1$ and $x' = 0$. As indicated by Eq. (3.9.8), and as alluded to above, this signals

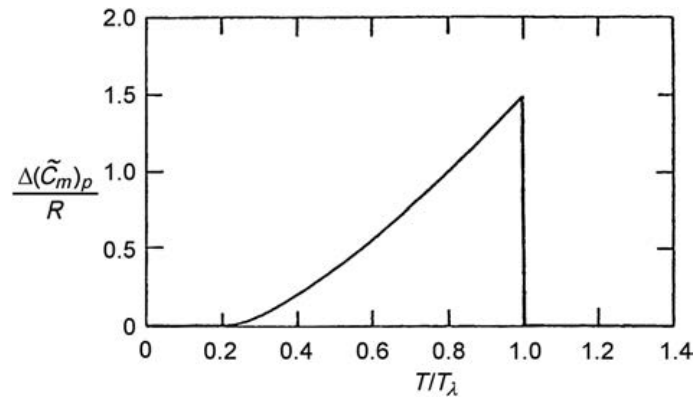


FIGURE 3.9.5

Plot of reduced heat capacity vs reduced temperature as obtained from Figure 3.9.4 with $w = 2R$.

the separation of the AB mixture into pure A and pure B—the completely ordered state of the system. With rising T , s_p drops slightly; x' and x'' move away from 0 and 1, respectively: some B has dissolved into A and vice versa. The system has now become slightly disordered. With an additional increase in T , s_p becomes still smaller; x' and x'' move further away from their end points, so that the two phases are now characterized by a greater degree of mixing and disorder. Finally, at T_λ , $s_p = 0$ and $x' = x'' = 1/2$. The two phases have merged into one and the mixing of the two components is complete. Thus, the decline in s_p from 1 to 0 is a measure of the increasing intermixing of components A and B in the two phases. Correspondingly, $\Delta\tilde{G}_m$, $\Delta\tilde{H}_m$, and $\Delta\tilde{C}_{pm}$ indicate the changes in Gibbs free energy, enthalpy, and heat capacity at constant pressure that are associated with each stage of the gradual transition from complete phase separation at $T = 0$ to complete mixing at $T = T_\lambda$.

Although these results were derived for binary solutions, the above formulation is of much more general applicability. As an example, consider a ferromagnetic domain in a specimen held at $T = 0$. All spins are aligned in one specific direction, with spins “up”. States with spin “down” do not exist. With rising temperature, some spin reversals are encountered; the system has become somewhat disordered. There is a progressive shift of this type with increasing T until, at the Curie temperature, there are an equal number of spins in either alignment distributed at random over the entire lattice. The material has entered the paramagnetic state. Another illustration is furnished by the adsorption of N atoms of Hg on $2N$ surface sites of an inert solid. At $T = 0$, the N Hg atoms are congregated on N adjacent sites as a cluster; the remaining N sites form an empty cluster. With a progressive rise in temperature, Hg atoms start to move onto previously empty sites, thereby diminishing the degree of ordering. Beyond a certain characteristic temperature, the Hg atoms tend to become randomly distributed, corresponding to complete disordering of the adsorbed atoms among available sites.

These examples show that a variety of physical situations can be treated by the present approach, namely cases involving a system in one of the two possible configurations: A or B, full or empty, up or down, plus or minus, and so on. These results again follow as an inescapable consequence from very modest beginnings, namely, the Margules formulation for activity coefficients in binary solutions. However, as with any elementary approach involving the use of many simplifying assumptions, one cannot expect quantitative agreement with experiment. The present approach, referred to as a *mean field theory*, neglects fluctuation phenomena that become prominent in handling higher order

transitions, especially near the critical point; see Chapters 1 and 7. However, the basic correctness of the theory shows that the overall approach is sound.

Extension of the Model

At first glance, it may appear as though the assumption regarding the equality of $w(T)$ for the two phases $'$ and $''$ in Eqs. (3.9.4a) and (3.9.4b) were excessively restrictive. It turns out, however, that when w is replaced by w_1 and by w_2 in Eqs. (3.9.4a) and (3.9.4b), respectively, one again recovers Eq. (3.9.8), except that in place of $w(T)$, one must now substitute $w_1(T) + f(T)\{w_2(T) - w_1(T)\} \equiv \omega(T)$ ⁴. Thus, the original T -dependent parametric function $w(T)$ is replaced by the more elaborate $\omega(T)$; however, the basic functional dependence of \tilde{G}/RT on x'' remains unaffected. Thus, the simple model developed in Eq. (3.9.7) *ff.* remains applicable when the restrictive assumption is relaxed as shown above.

Application of the Flory–Huggins Model

Calculations similar to those dealt with so far become rather involved when applied to the Flory–Huggins model and will not be developed in detail, but have been published and are also available upon request.⁵ Basically, one must first specify the composition x for component B *in the homogeneous phase* and specify the asymmetry parameter r . One then obtains a series of plots of the Gibbs free energies, Eq. (3.8.24), for various w/RT , whose minima correspond to the end points, $x' \leq x \leq x''$ over which the biphasic regions extend for each choice of w/RT ; special methods are introduced for their

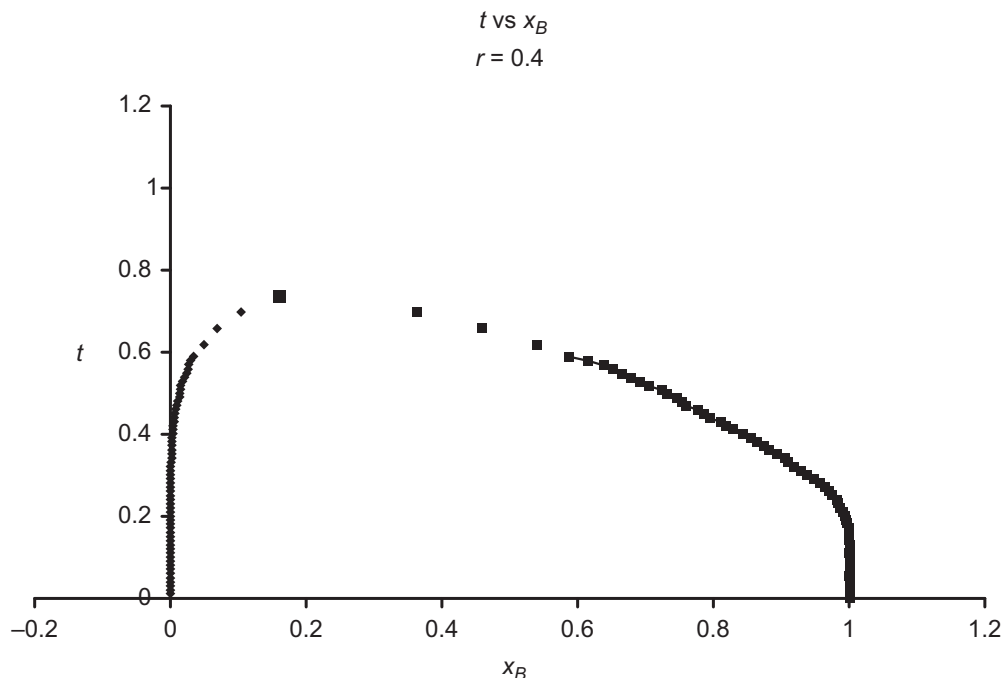


FIGURE 3.9.6

Phase diagram derived for the Flory–Huggins model; $t \equiv RT/w$, $r \equiv \tilde{V}_A^0/\tilde{V}_B^0$. Note the distortion relative to Figure 3.9.2. The square locates the maximum; above this reduced temperature, only the liquid phase is stable.

accurate determination. This permits the determination of f values via Eq. (3.9.3) and provides the inputs for the phase diagram shown in Figure 3.9.6 for the case $r = 0.4$.⁵ The enthalpy for each of the phases in equilibrium is found from Eq. (3.8.26) at the compositions $x \equiv x'_B$ and $x'' \equiv x''_B$, and their sum is determined by weighting with the factors $1 - f$ and f , respectively. Representative enthalpy curves are displayed in Figure 3.9.7 for the indicated choices of parameters. The slopes of these curves yield the heat capacities of interest; representative examples are shown in Figure 3.9.8.

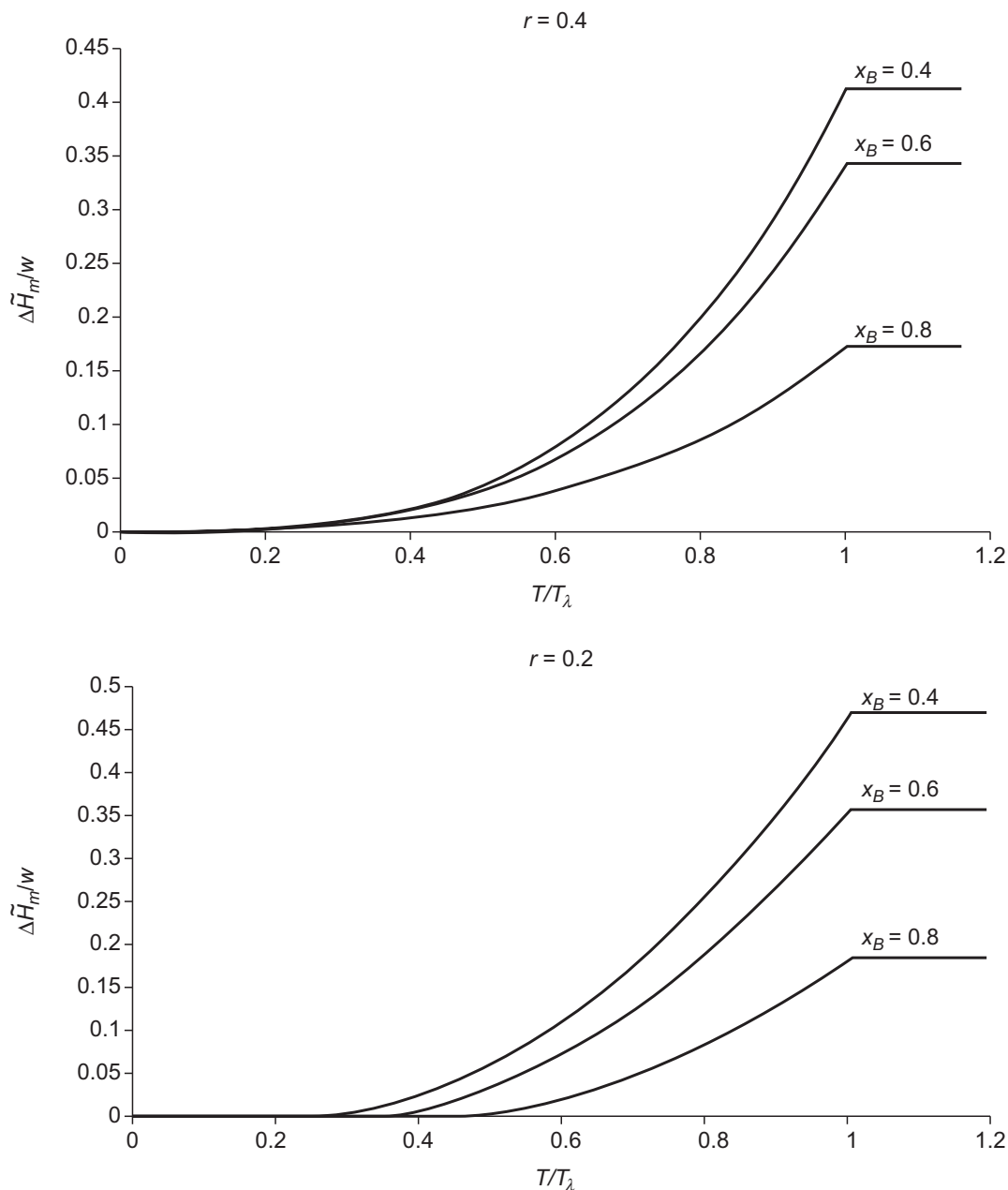


FIGURE 3.9.7

Plots of $\Delta \tilde{H}_m/w$ vs T/T_λ , showing how the scaled enthalpy of mixing varies with scaled temperature for various indicated parameters.

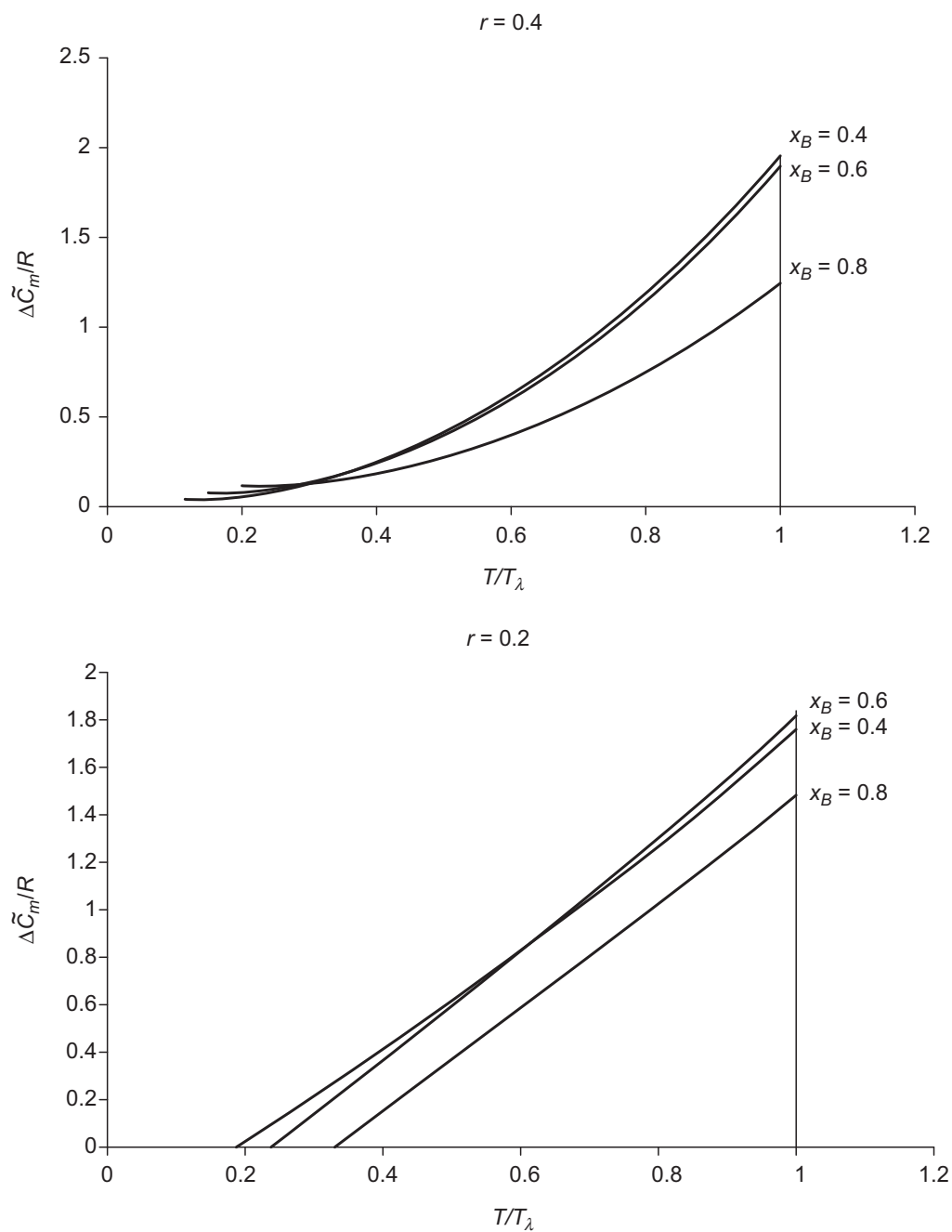


FIGURE 3.9.8

Plots of scaled heat capacities vs scaled temperature derived from Figure 3.9.7.

The phase diagram Figure 3.9.6 exhibits a skewed phase boundary but otherwise does not differ markedly from the comparable diagram in Figure 3.9.2. Likewise, the heat capacity curves do not differ greatly from the one displayed in Figure 3.9.5. Thus, the differences introduced by use of the Flory–Huggins model represent a modest improvement over the results of the Bragg–Williams approach.

Exercises and References

- 3.9.1. Correlate Figure 3.9.3 with Figure 3.9.2.
- 3.9.2. Why is the enthalpy of mixing almost zero at low temperatures, as in Figure 3.9.4, and why does it rise sharply as T approaches T_λ ?
- 3.9.3. Determine the entropy of mixing as a function of temperature, and sketch the resulting curve. Keep track of all approximations you make. Comment on your results.
- 3.9.4. I am indebted to Mr Joseph Roswarski of Purdue University for this derivation. Verify the claim.
- 3.9.5. The calculations leading to Figures. 3.9.6–3.9.8, based on the Flory–Huggins model, were performed by Mr Ross Hoehn of Purdue University as part of an undergraduate research project, including other choices of the r parameter. See also Ross Hoehn and J.M. Honig, *The Icfai University Journal of Chemistry*, **2**, 7–21 (2009). Requests for more extensive calculations should be addressed to jmh@purdue.edu.

3.10 Elements of Order–Disorder Theory and Applications

Introductory Comments

Closely related to the above discussion are elements of the so-called order–disorder theory; some of the numerous applications overlap with our earlier discussions, but nevertheless deserve a separate display. The presentation is a simplified version of original work by Hijmans and de Boer.¹ We couch the subsequent discussion in terms of a binary alloy system involving constituents A and B, distributed over a set of regularly spaced lattice sites, large enough in number that edge effects may safely be neglected. At the end, we generalize this approach. Ordinarily, interactions between constituents (particularly those of electrostatic origin) cover distances that are large compared to the lattice spacing. Then the probability of encountering a given constituent on a representative site depends on the state of occupation of a host of other sites, leading to an overwhelmingly complicated theoretical analysis. To simplify matters, we replace the actual lattice by a set of simpler, independent collections, termed *lattice arrays*; each array consists of a small assemblage of lattice points that mimic a subset of the lattice. For example, one may represent the lattice by an assemblage of points, plus bonds, triangles, squares, hexagons, and yet larger arrays, but the various individual units are of sufficiently small size that only a limited number of microvariables are required for a complete description of their statistical properties.

The problem then resolves itself to a decomposition of the lattice into these simpler figures, such that all lattice properties are optimally represented by the arrays. Here we shall concentrate on the simplest nontrivial version, whereby only nearest neighbor interactions are taken into account. Hopefully, since these are the strongest, we can get a reasonable approximation to the properties of the lattice.

Table 3.10.I Lattice Site Representations

Occupation Probability	Figure Representation	Designation	Total in Each Set	Energy Parameters
α_0	○	A	$(1 - Z)L\alpha_0$	ϵ_A
α_1	●	B	$(1 - Z)L\alpha_1$	ϵ_B
β_0	○ ○	A A	$(ZL/2)\beta_0$	ϵ_{AA}
β_1	○ ●	A B	$(ZL/2)\beta_1$	ϵ_{AB}
β_1	● ○	B A	$(ZL/2)\beta_1$	ϵ_{BA}
β_2	● ●	B B	$(ZL/2)\beta_2$	ϵ_{BB}

The Quasi-chemical Approximation

In this approach, we represent the lattice by a collection of *bonds* (b) which contains lattice *points* (a) as a subfigure; these units are depicted in Table 3.10.I. Let Z denotes the number of nearest neighbors to every lattice site; then from every one of the L lattice sites there emanate Z bonds, each of which terminates in two points. To prevent an overcount, we therefore populate the bond figure assembly with $(Z/2)L$ units. This collection already contains ZL points, while the correct count for the lattice is only L . To eliminate this overcount, we introduce a subarray of $(1 - Z)L$ points, so that the sum of the two arrays properly represents the lattice to this (low) degree of approximation. That the second assembly contains a negative number of units need cause no concern: one may alternatively consider the point array to consist of a positive number of constituents and then subtract their physical properties from those of the bond array—our approach is simply an equivalent operation.

The next step consists in specifying the possible *configurations* or *occupation states* of the above figure assemblies; here the termini of the bonds or the points themselves are either in state A or state B. As shown in Table 3.10.I, we characterize the BB, AB, BA, and AA bond configurations by the *distribution probabilities* $\beta_2, \beta_1, \beta_1$, and β_0 , respectively, and by the corresponding energies $\epsilon_{BB}, \epsilon_{AB}, \epsilon_{BA}$, and ϵ_{AA} . Similarly, members of the point assembly in states B and A are characterized by probabilities α_1, α_0 , and by energies ϵ_B, ϵ_A .

The above probabilities are subject to the following constraints:

$$\begin{aligned}\alpha_0 + \alpha_1 &= 1 \\ \beta_0 + 2\beta_1 + \beta_2 &= 1 \\ \alpha_1 &= \beta_1 + \beta_2.\end{aligned}\tag{3.10.1}$$

The first two relations represent the *normalization* requirements for probabilities. The last expression is a *consistency condition*: the number of sites encountered in the B state, as contained in the $(ZL/2)$ bonds and in the $(1 - Z)L$ point arrays, must match the actual number, $L\alpha_1$, of B sites in the lattice proper.

We can now specify the energy of the figure assemblies as shown below:

$$E = L[(Z/2)(\beta_0\epsilon_{AA} + 2\beta_1\epsilon_{AB} + \beta_2\epsilon_{BB}) + (1 - Z)(\alpha_0\epsilon_A + \alpha_1\epsilon_B)]. \quad (\epsilon_{AB} = \epsilon_{BA}). \tag{3.10.2}$$

The entropy relation is based on the number of statistical configurations pertinent to the figure assemblies (Sections 10.1 and 10.5):

$$W = \frac{(ZL/2)!}{(\beta_0 ZL/2)!(\beta_1 ZL/2)!^2(\beta_2 ZL/2)!} \cdot \frac{(1-Z)L!}{[\alpha_0(1-Z)L]![\alpha_1(1-Z)L]!}. \quad (3.10.3)$$

We then introduce the Boltzmann relation for the entropy as $S = k_B \ln W$. On taking logarithms of the above expression and introducing Stirling's approximation, $\ln N! \approx N \ln N - N$ for sufficiently large N , we find that

$$\begin{aligned} \ln W = & (ZL/2)\ln(ZL/2) - (\beta_0 ZL/2)\ln(\beta_0 ZL/2) - 2(\beta_1 ZL/2)\ln(\beta_1 ZL/2) - (\beta_2 ZL/2)\ln(\beta_2 ZL/2) \\ & + (1-Z)L \ln(1-Z)L - \alpha_0(1-Z)L \ln \alpha_0(1-Z)L - \alpha_1(1-Z)L \ln \alpha_1(1-Z)L. \end{aligned} \quad (3.10.4)$$

The nonlogarithmic terms have cancelled out. If logarithmic terms that involve solely the factor $\ln L$ are now separated out, further cancellations occur, and one is left with

$$S = -k_B L \{ (Z/2)(\beta_0 \ln \beta_0 + 2\beta_1 \ln \beta_1 + \beta_2 \ln \beta_2) + (1-Z)(\alpha_0 \ln \alpha_0 + \alpha_1 \ln \alpha_1) \}. \quad (3.10.5)$$

The above energy and entropy relations are deemed to be a reasonable approximation for those of the lattice proper. Clearly this is often questionable, but the above may serve as a first order approximation.

One may now combine Eqs. (3.10.2) and (3.10.5) to generate the Helmholtz free energy, $A = E - TS$, which must then be minimized to determine the equilibrium configurations for the alloy system. Because of the relations (3.10.1), only two of the five probabilities are independent; let us arbitrarily choose these to be α_1 and β_2 , so that

$$\alpha_0 = 1 - \alpha_1; \quad \beta_1 = \alpha_1 - \beta_2; \quad \beta_0 = 1 - 2\alpha_1 + \beta_2. \quad (3.10.6)$$

Then the determination of the chemical potential μ_s for the alloy system and the minimization of A at constant temperature proceeds along the following lines:

$$\begin{aligned} \frac{1}{L} \left[\frac{\partial A}{\partial \alpha_1} + \frac{\partial A}{\partial \alpha_0} \frac{\partial \alpha_0}{\partial \alpha_1} + \frac{\partial A}{\partial \beta_0} \frac{\partial \beta_0}{\partial \alpha_1} + \frac{\partial A}{\partial \beta_1} \frac{\partial \beta_1}{\partial \alpha_1} \right] &= \mu_s, \\ \frac{\partial A}{\partial \beta_2} + \frac{\partial A}{\partial \beta_1} \frac{\partial \beta_1}{\partial \beta_2} + \frac{\partial A}{\partial \beta_0} \frac{\partial \beta_0}{\partial \beta_2} &= 0. \end{aligned} \quad (3.10.7)$$

We substitute from Eqs. (3.10.2) and (3.10.5) and carry out the required differentiations, to obtain

$$\begin{aligned} (1-Z)[(\epsilon_B - \epsilon_A) + k_B T(\ln \alpha_1 - \ln \alpha_0)] + Z[(\epsilon_{AB} - \epsilon_{AA}) + k_B T(\ln \beta_1 - \ln \beta_0)] &= \mu_s, \\ (Z/2)[(\epsilon_{AA} - 2\epsilon_{AB} + \epsilon_{BB}) + k_B T(\ln \beta_0 - 2 \ln \beta_1 + \ln \beta_2)] &= 0. \end{aligned} \quad (3.10.8)$$

In the alloy problem under discussion, α_0 and α_1 are fixed by the composition of the material, and thus remain as parameters. The equilibrium state as provided by the second expression has the following form:

$$\frac{\beta_0\beta_2}{\beta_1^2} = \exp\left\{\frac{(2\varepsilon_{AB} - \varepsilon_{BB} - \varepsilon_{AA})}{k_B T}\right\} \equiv K_e. \quad (3.10.9)$$

Notice that the above is in the form of an “equilibrium constant” for the quasi-chemical reaction $2AB \rightarrow AA + BB$, hence the name.

We now substitute from Eq. (3.10.6) in Eq. (3.10.9) to solve for β_1 in terms of α_1 and α_0 to find

$$\beta_1 = \frac{-1 \pm \sqrt{1 + 4(K_e - 1)\alpha_0\alpha_1}}{2(K_e - 1)}. \quad (3.10.10)$$

With K_e in the range $[0, \infty]$, and $\beta_1, \alpha_0, \alpha_1$ required to be in the range $[0, 1]$, we must adopt the positive sign. Equation (3.10.10) shows that β_1 as a function of α_1 has a maximum and is symmetric about the α_1 midpoint at 0.5.

Limiting Cases

Several limiting cases are of interest: As K_e is increased indefinitely, β_1 approaches zero, so that the AB configuration tends to be absent; now, the abundance of AA and BB bonds indicates clustering of like species and phase aggregation. Conversely, as K_e approaches unity, one may expand the square root to first-order terms to find $\beta_1 = \alpha_0\alpha_1$; $\beta_0 = \alpha_0^2$; $\beta_2 = \alpha_1^2$; the various bond probabilities are now roughly equal, so that a more or less random distribution of A and B species is anticipated, reflecting the fact that the various energies ε are nearly identical.

For the case where K_e nearly vanishes, we must distinguish between the ranges $0 < \alpha_1 < 0.5$ and $0.5 < \alpha_1 < 1$. Then $\beta_1 = \alpha_1$; $\beta_0 = 0$; $\beta_2 = 1 - 2\alpha_1$ in the latter case, and $\beta_1 = 1 - \alpha_1$; $\beta_0 = 0$; $\beta_2 = 2\alpha_1 - 1$ in the former. These results are reasonable: in the present approximation, ε_{AB} is highly negative, pointing to strong attractive interactions between opposite species, to the near exclusion of AA or BB configurations if A and B are present in equal amounts. Under these conditions, A and B are surrounded by their opposites. When A and B differ in amounts, the majority component is left over, resulting in nonzero values for either β_0 or β_2 .

Gas Adsorption Processes

The order–disorder theory can immediately be applied to the adsorption of gases as a monolayer on the surface of a solid that equilibrates with the gas. Here A and B designate a surface site that is empty or covered by a molecule transferred from the gas to the solid. We begin with a simplified version in which we neglect lateral interactions between adsorbed molecules, thus allowing us to ignore the bond figure assemblies. At equilibrium, the chemical potential of the adsorbed phase, μ_s , matches that of the ideal gas at pressure P , namely $\mu_g = \mu_0 + RT \ln P$. Here μ_s is specified by the simplified version of Eq. (3.10.8) in which the β variables are missing and $z = 0$. On setting $\mu_s = \mu_g$ one may solve for

$$RT \ln(\alpha_1/\alpha_0 P) = \mu_0 - (\varepsilon_B - \varepsilon_A) \equiv \tilde{K}(T). \quad (3.10.11)$$

It is conventional to designate by $\theta \equiv \alpha_1$, the fraction of filled surface sites. Equation (3.10.11) may then be recast in the form

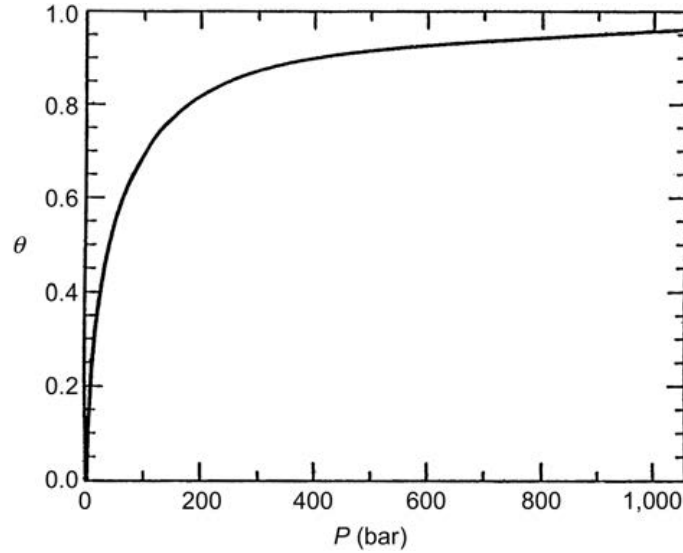


FIGURE 3.10.1

Plot of the Langmuir adsorption isotherm, Eq. (3.10.12); $K = 47.3$ bar.

$$\frac{\theta}{1 - \theta} = P e^{\tilde{K}(T)/RT} \equiv P/K_s(T); \text{ or } \theta = \frac{P}{P + K_s(T)}, \quad (3.10.12)$$

which is the famous *Langmuir adsorption isotherm* that governs the surface coverage as a function of the prevailing gas pressure at a fixed temperature T . A plot of θ vs P is displayed in Figure 3.10.1 for $K_s = 47.3$ bar. As is evident, θ first rises linearly with P and then saturates toward unity at high pressures. The temperature-dependent parameter involves the molar adsorption energy ($\epsilon_B - \epsilon_A$).

As the next, more advanced step, we include lateral interactions between gas molecules adsorbed on nearest neighbor sites, which requires inclusion of the bond figure assembly. The chemical potential, as specified by Eq. (3.10.8), is equated with that of the ideal gas: $\mu_s = \mu^0 + RT \ln P$. This leads to the following relation:

$$\begin{aligned} RT \ln C(T) &\equiv -\mu^0 + (1 - Z)(\epsilon_B - \epsilon_A) + Z(\epsilon_{AB} - \epsilon_{AA}) \\ &= RT \left\{ \ln P - (1 - Z) \ln \left(\frac{\alpha_1}{\alpha_0} \right) - Z \ln \left(\frac{\beta_1}{\beta_0} \right) \right\}, \end{aligned} \quad (3.10.13)$$

which may be rewritten as

$$P = C(T) \left[(\beta_1/\beta_0)^Z (\alpha_0/\alpha_1)^{(Z-1)} \right]. \quad (3.10.14)$$

We now set $\beta_1/\beta_0 = Qa$, $Q \equiv (P/Ca)^{1/Z}$, $a \equiv \alpha_1/\alpha_0$, so that Eq. (3.10.9) reads $\beta_2/\beta_0 = C(Qa)^2$; then

$$a = \frac{\alpha_1}{\alpha_0} = \frac{\beta_1 + \beta_2}{\beta_1 + \beta_0} = \frac{\beta_1/\beta_0 + \beta_2/\beta_0}{1 + \beta_1/\beta_0} = \frac{Qa(1 + CQa)}{1 + Qa}. \quad (3.10.15)$$

This expression turns into a polynomial in Q :

$$CaQ^2 + (1-a)Q - 1 = 0, \quad (3.10.16)$$

with the solutions

$$Q = \left[a - 1 \pm \sqrt{(1-a)^2 + 4Ca} \right] / 2Ca = \left[2\alpha_1 - 1 \pm \sqrt{1 + 4\alpha_1(1-\alpha_1)(C-1)} \right] / 2C\alpha_1. \quad (3.10.17a)$$

We ignore the minus sign as physically meaningless, reintroduce $\theta = \alpha_1$, then replace the square root with the symbol,

$$S \equiv \sqrt{1 + 4\theta(1-\theta)(C-1)}, \quad (3.10.17b)$$

and set

$$Q \equiv (S - 1 + 2\theta) / 2C\theta, \quad (3.10.17c)$$

so that Eq. (3.10.14) may be reformulated as

$$\frac{\beta_1}{\beta_0} = \left(\frac{P\alpha_0}{C\alpha_1} \right)^{1/Z} \frac{\alpha_1}{\alpha_0} = Qa. \quad (3.10.18)$$

The above reexpresses β_1/β_0 in terms of a and P . We can then substitute Eqs. (3.10.17a, 3.10.17b, 3.10.18) into Eq. (3.10.14) to set up the final relation of interest:

$$\frac{P}{C} = \frac{\theta}{1-\theta} \left(\frac{S-1+2\theta}{2\theta} \right)^Z \exp \left\{ \frac{Zw}{RT} \right\}; \quad C \equiv e^{-w/RT}; \quad w \equiv \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}. \quad (3.10.19)$$

The above represents the so-called *Fowler–Guggenheim adsorption isotherm* equation.² Numerical calculations indicate that for properly chosen C values portions of the isotherms show up as loops. As is familiar from the Maxwell constructions, this signals the onset of two-dimensional condensation, leading to discontinuities in θ ; i.e., at reduced pressures P_c , the surface coverage changes discontinuously from θ_1 to θ_2 . Again, at sufficiently high pressures, the monolayer coverage of the surface goes to unity. When C is reduced in value, the loops disappear; one obtains a distorted Langmuir isotherm that reduces to the latter when $C = 1$. The verification of this statement is left as an exercise.

Binary Solutions

We adapt the above theory to specify the thermodynamic properties of binary solutions, whether solid or liquid. The use of lattice theory to liquids may seem paradoxical; however, in considering fluid properties, one must distinguish between convection involving motion of the center of mass, and internal reconfigurations. The surroundings of a representative molecule in the liquid phase, even in convection, are a distorted version of those that prevail in the solid. Hence, as a rock-bottom approximation, it is not a travesty to apply lattice theories to the present case.

In conformity with standard practice, we deal with molar quantities, replacing k_B with the gas constant R . It is also appropriate to set $L\alpha_0 = N_A$, $L\alpha_1 = N_B$, so that the mole fractions of components A and B are given by $\alpha_i = N_i/(N_A + N_B)$, $i = A, B$. Observe that N_A and N_B may be independently

varied by alterations in composition (in contrast to the last section where, for every site that is filled, an empty one “disappears”), whence $L = N_A + N_B$ is no longer a fixed quantity.

The free energy of an ideal solution (wherein all interactions between molecules are ignored) is specified by

$$A_i = N_A \varepsilon_A + N_B \varepsilon_B + RT \ln \left\{ N_A \ln \frac{N_A}{N_A + N_B} + N_B \ln \frac{N_B}{N_A + N_B} \right\}, \quad (3.10.20)$$

where the first two terms relate to the energies of the isolated units A and B, and the remaining terms involve the entropy $S_i = -RL\{\alpha_0 \ln \alpha_0 + \alpha_1 \ln \alpha_1\}$. The chemical potential of B is found by differentiation of A_i with respect to N_B keeping N_A and T constant; at equilibrium, this must equal the chemical potential of B in the ideal gas phase. Accordingly,

$$\mu_g = \mu_0 + RT \ln P_B = \mu_B = \varepsilon_B + RT \ln [N_B / (N_A + N_B)] = \varepsilon_B + RT \ln \alpha_1. \quad (3.10.21)$$

which may be reformulated as $\ln (P_B / \alpha_1) = (\varepsilon_B - \mu_0) / RT$. On the other hand, for pure B, $\alpha_1 = 1, P_B = P_B^0$, where P_B^0 is the pressure of the gas in equilibrium with pure B. Then,

$$P_B = \alpha_1 P_B^0, \quad (3.10.22)$$

which is Raoult's Law.

We now take account of interactions between molecular units in the nearest-neighbor (bond) approximation. We rework the normalization and consistency conditions to set $\beta_2 = \alpha_1 - \beta_1$ and $\beta_0 = \alpha_0 - \beta_1$, except where these occur as logarithmic arguments, and then construct the Helmholtz free-energy expression from Eqs. (3.10.2) and (3.10.5). This leads to

$$\begin{aligned} A = & (1 - Z)L[\alpha_0 \varepsilon_A + \alpha_1 \varepsilon_B] + (ZL/2)[(\alpha_0 - \beta_1)\varepsilon_{AA} + 2\beta_1 \varepsilon_{AB} + (\alpha_1 - \beta_1)\varepsilon_{BB}] \\ & + RT \left\{ (1 - Z)L[\alpha_0 \ln \alpha_0 + \alpha_1 \ln \alpha_1] + (ZL/2)[(\alpha_0 - \beta_1) \ln \beta_0 \right. \\ & \left. + 2\beta_1 \ln \beta_1 + (\alpha_1 - \beta_1) \ln \beta_2] \right\}. \end{aligned} \quad (3.10.23)$$

Next, introduce the equilibrium constraint of Eq. (3.10.8) to eliminate terms that carry β_1 as a multiplier to write

$$\begin{aligned} A = & (1 - Z)L[\alpha_0 \varepsilon_A + \alpha_1 \varepsilon_B] + (ZL/2)[\alpha_0 \varepsilon_{AA} + \alpha_1 \varepsilon_{BB}] + RT \{ (ZL/2)[(\alpha_0 \ln(\alpha_0 - \beta_1)) \\ & + \alpha_1 \ln(\alpha_1 - \beta_1)] + (1 - Z)L[\alpha_0 \ln \alpha_0 + \alpha_1 \ln \alpha_1] \}. \end{aligned} \quad (3.10.24)$$

The above forms the starting point for determining the thermodynamic properties of binary solutions. Unfortunately, these relations become extremely unwieldy even in this approximation; you may access my notes for detailed derivations.³ Let us therefore introduce simplifications to minimize the mathematical labor without destroying the main features of first order theory. In this section, we define the interaction energy ϖ by

$$\varpi \equiv \varepsilon_{BB} + \varepsilon_{AA} - 2\varepsilon_{AB} = -RT \ln C, \quad (3.10.25)$$

and consider the case $\varpi / RT \ll 1$, or equivalently, $C - 1 \rightarrow 0$. We rewrite Eq. (3.10.9) in the form $(\alpha_0 - \beta_1)(\alpha_1 - \beta_1) / \beta_1^2 = C$, which is a quadratic equation in β_1 , with the solution

$$\beta_1 = \frac{S-1}{2(C-1)}, \quad S \equiv \sqrt{1+4\alpha_0\alpha_1(C-1)}. \quad (3.10.26)$$

We now expand to second-order terms the quantities

$$C-1 = e^{-\varpi/RT} - 1 = -\frac{\varpi}{RT} \left[1 - \frac{1}{2} \frac{\varpi}{RT} \right]; \quad S \approx 1 + 2\alpha_0\alpha_1(C-1) - 2\alpha_0^2\alpha_1^2(C-1)^2, \quad (3.10.27)$$

whence

$$\beta_1 \approx \alpha_0\alpha_1 - \alpha_0^2\alpha_1^2(C-1); \quad \alpha_0 - \beta_1 = \alpha_0^2[1 + \alpha_1^2(C-1)], \quad (3.10.28)$$

and

$$\ln(\alpha_0 - \beta_1) = 2 \ln \alpha_0 + \ln[1 + \alpha_1^2(C-1)] \approx 2 \ln \alpha_0 + \alpha_1^2(C-1). \quad (3.10.29)$$

Similarly,

$$\ln(\alpha_1 - \beta_1) \approx 2 \ln \alpha_1 + \alpha_0^2(C-1). \quad (3.10.30)$$

When these last two relations are substituted in Eq. (3.10.24), we obtain

$$\begin{aligned} A = & (1-Z)L[\alpha_0\varepsilon_A + \alpha_1\varepsilon_B] + (ZL/2)[\alpha_0\varepsilon_{AA} + \alpha_1\varepsilon_{BB}] \\ & + RT\{(ZL/2)[\alpha_0\alpha_1^2(C-1) + \alpha_1\alpha_0^2(C-1)] + \alpha_0 \ln \alpha_0 + \alpha_1 \ln \alpha_1\}. \end{aligned} \quad (3.10.31)$$

Now, set $\alpha_0\alpha_1^2(C-1) + \alpha_1\alpha_0^2(C-1) = \alpha_0\alpha_1(C-1) \approx -\alpha_0\alpha_1\varpi/RT$; when this relation is introduced into the above, we find that

$$\begin{aligned} A = & (1-Z)L[\alpha_0\varepsilon_A + \alpha_1\varepsilon_B] + (ZL/2)[\alpha_0\varepsilon_{AA} + \alpha_1\varepsilon_{BB}] \\ & + RTL\{\alpha_0 \ln \alpha_0 + \alpha_1 \ln \alpha_1 - \alpha_0\alpha_1 Z\varpi/2RT\}. \end{aligned} \quad (3.10.32)$$

At this stage, let us define $\chi_A \equiv (Z/2)(\varepsilon_{AA} - 2\varepsilon_A)$, $\chi_B \equiv (Z/2)(\varepsilon_{BB} - 2\varepsilon_B)$, and reintroduce N_A/L and N_B/L to replace α_0 and α_1 . This leads to the final formulation ($L = N_A + N_B$),

$$A = N_A\varepsilon_A + N_B\varepsilon_B + N_A\chi_A + N_B\chi_B + RT\left\{N_A \ln \frac{N_A}{N_A + N_B} + N_B \ln \frac{N_B}{N_A + N_B}\right\} - \frac{N_A N_B}{N_A + N_B} \frac{Z\varpi}{2}. \quad (3.10.33)$$

This expression provides all thermodynamic information of interest. For example, the chemical potential of species B in solution is specified by

$$\mu_B = \left(\frac{\partial A}{\partial N_B} \right)_{T, N_A} = \mu_B^0 + RT \ln \frac{N_B}{N_A + N_B} - \frac{Z\varpi}{2} \left(\frac{N_A}{N_A + N_B} \right)^2 = \mu_B^0 + RT \ln \alpha_1 - \frac{Z\varpi}{2} \alpha_0^2, \quad (3.10.34)$$

where $\mu_B^0 \equiv \mu_B(T, 0, N_B)$. Comparison with the standard thermodynamic formulation $\mu_B = \mu_B^0 + RT \ln x_B + RT \ln \Gamma_B$ shows that the activity coefficient for component B and the standard chemical potential are specified by

$$\ln \Gamma_B = -(Z\varpi/2RT)\alpha_0^2; \quad \mu_B^0 = \varepsilon_B + \chi_B. \quad (3.10.35)$$

Thus, in the current approximation, we have determined Γ and μ_B^0 —quantities that arise as parameters in thermodynamics—in terms of the energetics and the prevailing temperature of the solution. Raoult's law now gets modified to read

$$P_B = P_B^0 \alpha_1 e^{-\alpha_0^2 Z\varpi/2RT}, \quad (3.10.36)$$

while the free energy of mixing is specified by

$$A_m = RTL\{\alpha_0 \ln \alpha_0 + \alpha_1 \ln \alpha_1\} - L\alpha_0 \alpha_1 Z\varpi/2. \quad (3.10.37)$$

The first term represents the entropy of mixing, which coincides with that of the zero-order theory; the second term relates to the enthalpy of mixing. Mixtures satisfying the above criteria are said to be *strictly regular*. We had encountered this relation before in a somewhat different disguise in Section 3.8.

Ferromagnetism

The order–disorder formalism may also be adapted to the study of ferromagnetism, where atoms or molecules placed on a lattice with a net magnetic moment M may be aligned with or against (as in antiferromagnetism) an externally imposed magnetic field H . Here we introduce only the initial features of this approach. We include only exchange interactions between nearest neighbors, $-J/2$ if moments are parallel to each other, and $+J/2$ if they are oppositely directed. Then the energy of the system as specified by the bond and point figure assemblies, exclusive of the interactions with the magnetic field, are given by

$$E_1 = (1-Z)(\alpha_0 \varepsilon_A + \alpha_1 \varepsilon_B) + (ZL/2)\{\beta_0(-J/2 + \varepsilon_{AA}) + 2\beta_1(J/2 + \varepsilon_{AB}) + \beta_2(-J/2 + \varepsilon_{BB})\}, \quad (3.10.38)$$

while the magnetic field interaction is specified by

$$E_H = -\mathcal{M}\mathcal{H}L\{(Z/2)(2\beta_0 - 2\beta_2) + (1-Z)(\alpha_0 - \alpha_1)\} = -\mathcal{M}\mathcal{H}L(\alpha_0 - \alpha_1) \quad (3.10.39)$$

Note the introduction of negative signs for the BB bond and B point configurations, the absence of a term involving β_1 for which the magnetic moments cancel out, and the use of consistency relations to achieve the simplified version on the right. The total energy is specified by

$$E = (ZL/2)\{(J/2)(2\beta_2 - \beta_0 - \beta_2) + \beta_0 \varepsilon_{AA} + 2\beta_0 \varepsilon_{AB} + \beta_0 \varepsilon_{BB}\} - \mathcal{M}\mathcal{H}L(\alpha_0 - \alpha_1) + (1-Z)L[\alpha_0 \varepsilon_A + \alpha_1 \varepsilon_B]. \quad (3.10.40)$$

The entropy is still representable by Eq. (3.10.5), together with the equilibrium constraint (8) in the form

$$\beta_0 \beta_2 / \beta_1^2 = \exp\{2J - \varpi/RT\} \quad (3.10.41)$$

and

$$(\alpha_1/\alpha_0)^{Z-1}(\beta_0/\beta_2)^{Z/2} = \exp\{2\mathcal{M}\mathcal{H}/RT\}. \quad (3.10.42)$$

Beyond this point, one must proceed by standard theory; here, we have simply indicated how order–disorder theory may be applied to situations that seem far removed from the original concepts.

Intermediate Statistics

Here we employ order–disorder theory to derive expressions for the statistics of interacting fermions that generalize the conventional approach to the subject, as expressed by Fermi–Dirac statistics. This approach is taken from Ref. 4. Consider an assembly of lattice sites which are either empty, or are occupied by an electron in the spin-up or spin-down state, or which contain two electrons with paired spins. These configurations, which are the only ones allowed by the Pauli exclusion principle, are pictorially displayed in Table 3.10.II as various “bond” occupations, along with various different designations of occupation states, and as the corresponding energy parameters. Here $n_{i\uparrow}$ represents the occupancy of site i by an electron in the spin-up state, $\sigma = \uparrow, \downarrow$ represents the spin state, and the angular brackets stand for expectation values. *Note carefully* that, by contrast to our earlier practice, the bond figure here represents an *individual site*, with a capacity of up to two electrons. The bond configurations represent a *single lattice unit* in empty (AA), singly occupied (BA or AB), or doubly occupied (BB) configurations, with probabilities $\beta_0, \beta_{\uparrow}, \beta_{\downarrow}$, or β_2 , respectively. These probabilities, which will be treated somewhat differently from those considered so far, are not independent; they must add up to unity: in the absence of an externally applied magnetic field

$$\beta_0 + \beta_{\uparrow} + \beta_{\downarrow} + \beta_2 = 1, \quad \beta_1 \equiv \beta_{\uparrow} = \beta_{\downarrow}. \quad (3.10.43)$$

Also, the fraction of occupied and unoccupied sites, α_1 and α_0 , must add up to unity; $\alpha_0 + \alpha_1 = 1$. In addition, the occupation states are subject to the consistency condition (different from those encountered earlier)

$$2\alpha_1 = 2\beta_2 + \beta_{\uparrow} + \beta_{\downarrow}. \quad (3.10.44)$$

The latter states that the total number of occupied lattice sites, $\alpha_1 L$, must match the number specified by the bond and point occupancy states.

Because of the above constraints, the number of independent variables is reduced to two; we arbitrarily choose them to be α_1 and β_2 . Then,

$$\beta_1 = \alpha_1 - \beta_2, \quad \beta_0 = 1 - 2\alpha_1 + \beta_2. \quad (3.10.45)$$

For convenience, we set $\varepsilon_{AA} = 0$, $\varepsilon_{AB} = \varepsilon_{BA} \equiv \varepsilon$, whence the energy of the lattice constituency per site reads

$$E_b/L = \beta_2 \varepsilon_{BB} + 2\beta_1 \varepsilon + \beta_0 \varepsilon_{AA} \equiv U_H \beta_2 + 2\varepsilon \alpha_1; \quad \varepsilon_{BB} \equiv U_H + 2\varepsilon. \quad (3.10.46)$$

Here we have introduced U_H as the *Hubbard parameter* for the energy of interaction between two electrons residing on the same site.

Occupancy	Fermion Representation	Bond	Representation	Energy
Empty state	$\beta_0 = \langle (1 - n_{i\uparrow})(1 - n_{i\downarrow}) \rangle$	○ ○	A A	ε_{AA}
Single occupancy	$2\beta_1 = \sum_{\sigma} \langle n_{i\sigma} (1 - n_{i\bar{\sigma}}) \rangle$	○ ● ● ○	A B B A	ε_{AB} ε_{BA}
Double occupancy	$\beta_2 = \langle n_{i\uparrow} n_{i\downarrow} \rangle$	● ●	B B	ε_{BB}

The average reduced entropy per site is specified in the customary fashion by

$$\begin{aligned} -S_b/k_B L &= \beta_0 \ln \beta_0 + 2\beta_1 \ln \beta_1 + \beta_2 \ln \beta_2 \\ &= (1 - 2\alpha_1 + \beta_2) \ln(1 - 2\alpha_1 + \beta_2) + 2(\alpha_1 - \beta_2) \ln(\alpha_1 - \beta_2) + \beta_2 \ln \beta_2. \end{aligned} \quad (3.10.47)$$

We now construct the Helmholtz free energy $A_b = E_b - TS_b$ and enforce equilibrium conditions by minimizing the resultant with respect to β_2 . Straightforward mathematical operations yield

$$\frac{(1 - 2\alpha_1 + \beta_2)\beta_2}{(\alpha_1 - \beta_2)^2} \equiv \frac{\beta_2\beta_0}{\beta_1^2} = \exp\left\{\frac{-U_H}{k_B T}\right\} \equiv C. \quad (3.10.48)$$

The above once more represents the standard *quasi-chemical approximation* in the sense that the ratio of probabilities is derivable from the “quasi-chemical reaction” $2AB = AA + BB$, with C equivalent to the “equilibrium constant”.

The chemical potential μ of the electron assembly, otherwise known as the *Fermi energy*, is found by differentiation with respect to $\alpha_1 L$, the actual number of electrons distributed among the sites. Here, because of our somewhat unusual specification of site occupancies, one encounters a common factor of 2 throughout, that may be absorbed in the definition for μ (recall that the “bonds” with two termini actually refer to single electron spin states), so that

$$\mu = \frac{\partial(F_b/L)}{2\partial\alpha_1} = \varepsilon + k_B T \ln \frac{\alpha_1 - \beta_2}{1 - 2\alpha_1 + \beta_2}, \quad (3.10.49)$$

which may be rearranged as

$$\frac{\alpha_1 - \beta_2}{1 - 2\alpha_1 + \beta_2} = e^{-x}; \quad x \equiv \frac{\varepsilon - \mu}{k_B T}. \quad (3.10.50)$$

Thus, x represents the reduced electron energy relative to the Fermi level.

Now multiply Eqs. (3.10.48) and (3.10.50) to obtain

$$\alpha_1 = \beta_2(1 + e^x/C), \quad (3.10.51)$$

and insert this relation into Eq. (3.10.50) to obtain

$$\beta_2 = \frac{1}{1 + e^x(2 + e^x)/C}, \quad (3.10.52)$$

as well as the distribution function of interest:

$$\alpha_1 = \frac{1 + e^x/C}{1 + e^x(2 + e^x)/C}. \quad (3.10.53)$$

Equation (3.10.53) represents the fraction of all available sites that are occupied, and $1 - \alpha_1$ represents the fraction of sites that are empty. The distribution of occupancies between double and single and empty configurations is given by Eq. (3.10.52), and by

$$\beta_1 = \frac{e^x/C}{1 + e^x(2 + e^x)/C}; \quad \beta_0 = \frac{e^{2x}/C}{1 + e^x(2 + e^x)/C} \quad (3.10.54)$$

respectively.

Special Cases

Particular interest attaches to two distinct special cases: $C = 1$, corresponding to $U_H = 0$; there are no intra-atomic electron interactions. Then

$$\alpha_1 = \frac{1}{1 + e^x}; \quad (3.10.55)$$

i.e., we have recovered the Fermi distribution function. Actually, we have used only a single-energy parameter x , rather than a distribution of energy levels envisioned by Fermi. However, this parameter is arbitrarily variable, so that it does not prevent us from applying the above relation to freely variable energies. Conventionally this situation is handled by allowing ε to depend on a wave number vector \mathbf{k} . The various probabilities now depend on \mathbf{k} . The entire analysis carries through as before but the various thermodynamic quantities of interest are obtained by integrating over \mathbf{k} to obtain macroscopic properties.

As expected, under the complete randomization we also find

$$\beta_2 = (1 + e^x)^{-2} = \alpha_1^2; \quad \beta_1 = e^x / (1 + e^x)^2 = \alpha_1 \alpha_0; \quad \beta_0 = e^{2x} / (1 + e^x)^2 = \alpha_0^2. \quad (3.10.56)$$

Of equal interest is the opposite case $C = 0$, corresponding to an infinite repulsion energy between two electrons on the same site. Now, as expected, $\beta_2 = 0$; no doubly occupied sites are encountered; also,

$$\alpha_1 = \beta_1 = \frac{1}{2 + e^x}; \quad \beta_{\uparrow} = \beta_{\downarrow} = \frac{1}{1 + e^{x/2}}, \quad (3.10.57)$$

which corresponds to electron distribution for impurity centers in semiconductors associated with energy ε relative to the Fermi level, when dealing with strongly interacting electrons.

Lastly,

$$\beta_0 = e^x / (2 + e^x). \quad (3.10.58)$$

General Discussion

For the general case, $0 < U_H < \infty$, we must distinguish between three different situations:

- (i) $\varepsilon - \mu + U_H < 0$; $\varepsilon - \mu < 0$: In this range at $T = 0$, $\beta_2 = 1$, $\beta_1 = \beta_0 = 0$; all electrons settle in the level of energy ε in the paired-spin configuration.
- (ii) $\varepsilon - \mu + U_H > 0$; $\varepsilon - \mu < 0$. Now, at $T = 0$, $\beta_1 = 1$, $\beta_2 = \beta_0 = 0$; all the electrons occupy the sites singly in either the spin-up or in the spin-down configuration.
- (iii) $\varepsilon - \mu + U_H > 0$; $\varepsilon - \mu > 0$: Now at $T = 0$, $\beta_0 = 1$, and $\beta_1 = \beta_2 = \alpha_1 = 0$; no excited states in this energy range are occupied by electrons; all electrons congregate or condense in the lowest allowed configuration.

Discussion

We note that order-disorder theory provides a unified description for a variety of phenomena that come under the umbrella of organizational problems. It is in principle a simple matter to extend the

Hijmans–de Boer methodology to include more extended representative arrays such as triangles, squares, hexagons, and so on. However, one soon gets bogged down in an enormous conglomeration of occupation states and parameters, without significantly improving on the characterization of the physical properties of materials. If you are interested in how to proceed please consult Ref. 1.

References

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Thermodynamic Properties of Electrolytes and of EMF Cells

4

4.0 Introductory Comments

In this chapter, we study the thermodynamic properties of ionic solutions, where the interaction forces between charged species are both strong and of long range. At the outset we need to take account of deviations from ideality, using the machinery set up in the first half of Chapter 3, in which the concept of activity and activity coefficients plays an important part. Heavy reliance is therefore placed on the Debye–Hückel theory, which is used below without justification. The proper derivation is postponed to Chapter 9, because the lengthy analysis interferes with the exposition of the main points to be made here. The second part of this chapter deals with galvanic cells. Here, the emphasis is on fundamentals and on how such cells may be used to study thermodynamic processes. For the myriad applications, special uses, or refined specializations you need to consult monographs and review papers in the field.

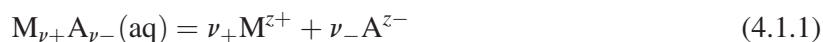
4.1 Activities of Strong Electrolytes

In 1884 Svante Arrhenius advanced the then very revolutionary hypothesis that ionic crystals dissolved in aqueous solutions tend to ionize partially or completely. That this should be the case may be rationalized by noting that electronic interactions are greatly weakened through the immersion of such crystals in water with its large dielectric constant. This effectively loosens the cohesive forces that hold the crystal together.

The ionization process may be represented by an “equation” of the form $M_{\nu+}A_{\nu-}(\text{aq}) = \nu_+M^{z+} + \nu_-A^{z-}$ where M and A represent the cationic and anionic constituent, z_+ and z_- are their respective ionic charges, and ν_+ and ν_- , the corresponding stoichiometry numbers. In the above ionization process $M_{\nu+}A_{\nu-}$ represents either a dissolved species that is equilibrated with the undissolved compound in a saturated solution as well as with the ionized species, or that exists as a dissolved compound in an unsaturated solution. The above representation conceals a multitude of complexities: in most cases the solution process is far more involved than shown. For example, in the ionization of AgI one encounters the aqueous species AgI, Ag^+ , I^- , AgI_2^- , Ag_2I^+ , and several more exotic combinations. Nevertheless, (fortunately) what matters in thermodynamics is the net process of interest, involving here the ionic species Ag^+ and I^- .

Chemical Potential of Ionized Species; Mean Activities

We first need to specify the chemical potential of ionized species. Corresponding to the schematic ionization reaction



the overall chemical potential is specified by

$$\Delta G_d = \sum_i \nu_i \mu_i = \nu_{i+} \mu_{i+} + \nu_{i-} \mu_{i-} - \mu_i, \quad (4.1.2a)$$

where μ_i is the chemical potential of the undissolved salt or undissociated compound of species i , $M_{\nu+}A_{\nu-}$. At chemical equilibrium, ΔG_d vanishes, so that for a given species i

$$\mu_i = \nu_{i+} \mu_{i+} + \nu_{i-} \mu_{i-}. \quad (4.1.2b)$$

We now introduce the conventional equation $\mu_i = \mu_i^*(T, 1) + \ln a_i(T, P, x_i)$ for the neutral species, as developed in Chapter 3, and apply this formulation as well to the ionized units. Then Eq. (4.1.2b) reads

$$\mu = \mu^* + RT \ln a = (\nu_+ \mu_+^* + \nu_- \mu_-^*) + RT(\nu_+ \ln a_+ + \nu_- \ln a_-), \quad (4.1.3a)$$

where the subscript i and the arguments of the various functions have been temporarily dropped to avoid proliferation of symbols. If Eq. (4.1.3a) is to be rewritten in the form (4.1.2b), the two sides of Eq. (4.1.3a) must match. We set

$$\mu^* \equiv \nu_+ \mu_+^* + \nu_- \mu_-^*, \quad (4.1.3b)$$

as the *standard chemical potential* for dissolved ionized species. For consistency we also adopt a *mean relative activity* by the relation

$$a \equiv a_+^{\nu_+} = (a_+)^{\nu_+} (a_-)^{\nu_-}, \quad (4.1.3c)$$

which allows us to write Eq. (4.1.3a) in the more compact form

$$\mu_i = \mu_i^* + RT \ln[(a_{i+})^{\nu_+} (a_{i-})^{\nu_-}] = \mu_i^*(T, P) + \nu_i RT \ln a_{i\pm}(T, P, x_i), \quad (4.1.4)$$

while setting

$$\nu_i \equiv \nu_{i+} + \nu_{i-}. \quad (4.1.5)$$

Relation (4.1.3c) is also motivated by considering as an example the dissociation of $\text{CaCl}_2 = \text{Ca}^{2+} + 2\text{Cl}^-$. The ionic molalities are given by $m_+ = m$ and $m_- = 2m$. The geometric mean of these concentrations leads to the relation $m_{\pm}^3 = m_+ m_-^2 = 4m^3$. A similar relationship obviously holds for the activities.

Equations (4.1.3–4.1.5) imply more than meets the eye. First, one must always satisfy the *law of electroneutrality*, according to which (with $z_- < 0$),

$$\nu_+ z_+ + \nu_- z_- = \nu_+ z_+ - \nu_- |z_-| = 0. \quad (4.1.6a)$$

Second, there is no possibility of separately determining either a_+ or a_- . For, by definition, $\mu_+ = (\partial G / \partial n_+)_{T, P, n_-}$; that is, the determination of μ_+ requires addition of only positive ions to the solution at constant T and P , while holding the concentration of anions fixed. Such a step violates the law of electroneutrality and cannot be carried out operationally. Thus, it is experimentally not meaningful to deal with individual ionic activities; rather, as Eq. (4.1.3c) shows, only their geometric mean, or the corresponding logarithmic sum, is the appropriate choice as the independent variable. Third, since thermodynamic descriptions must be confined to measurable properties we may regard

the quantity $\mu^* + RT \ln a$ on the left of Eq. (4.1.3a) as an “effective chemical potential” that governs the properties of electrolytes. On the other hand, one does not wish to ignore the ionic nature of the solution; hence, it is customary to write

$$\mu_i = \mu_i^*(T, P) + RT \ln a_{i\pm}(T, P, x_i)^{\nu_i}, \quad (4.1.6b)$$

which is in consonance with Eq. (4.1.4).

Mean Concentrations and Activity Coefficients

Fourth, one must refer the activity a or a_{\pm}^{ν} to a measurable quantity in an ideal solution. For this purpose we set up a relation analogous to Eq. (4.1.3c), namely,

$$x_i = (x_{i\pm})^{\nu_i} = (x_{i+})^{\nu_{i+}} (x_{i-})^{\nu_{i-}}. \quad (4.1.7)$$

Here, for completely ionized solutes we define the mole fraction for the i th positively charged species in solution by $x_{i+} = n_{i+} / \sum_s \nu_s n_s$, where the index s runs over all distinct *chemical* compounds added to the aqueous phase, not over the ionic species i present in the solution. The dissociation process of these compounds in water is attended to by insertion of the sum $\nu_s = \nu_{s+} + \nu_{s-}$, with ν_{s+} or ν_{s-} , the number of cations or anions per formula unit of the s th species $M_{\nu+}A_{\nu-}$. Thus, on complete ionization, each mole of the compound $M_{\nu+}A_{\nu-}$ yields $(\nu_+ + \nu_-) = \nu$ moles of ions in solution.

We now introduce mean activity coefficients

$$(\Gamma_{i\pm})^{\nu_i} = (\Gamma_{i+})^{\nu_{i+}} (\Gamma_{i-})^{\nu_{i-}}, \quad (4.1.8)$$

in strict analogy with Eq. (4.1.7); here $\Gamma_{i\pm} = \Gamma_{i\pm}(T, P, x_{i\pm})$. It should then be clear that the relation between activity and activity coefficient that supplants Eq. (3.3.9) now reads (omitting subscripts i for simplicity)

$$a_{\pm}(T, P, x_{\pm}) = \Gamma_{\pm}(T, P, x_{\pm}) x_{\pm}. \quad (4.1.9)$$

Henry's Law as Applied to Ionic Solutions in Equilibrium with Gases

To determine the relevant activities or activity coefficients one proceeds by analogy to Section 3.6, in invoking Henry's law. If the undissociated compound is volatile (such as HCl) the activity coefficient relative to molality, Γ_+ or Γ_- , is introduced; the equilibrium between the gaseous species at activity a_g and the completely ionized unit in solution leads to the equilibrium constraint

$$K_H = \frac{a_g}{(\nu_+ m)(\nu_- m) \Gamma_{\pm}^{\nu}}, \quad (4.1.10)$$

where at least in sufficiently dilute solutions one may set $a_g = P_g$. Also, in solutions where the linearity of Henry's law holds, $\Gamma_{\pm}^{\nu} = 1$, with $P^{\wedge} = K_H$ being the extrapolated pressure corresponding to $m = 1$. In these circumstances

$$P_g = P^{\wedge} (\nu_+ \nu_-) m^2, \quad (4.1.11)$$

so that a plot of P_g vs m^2 is linear. Once P^{\wedge} has been determined Eq. (4.1.10) may be used to find the mean activity coefficient of the volatile substance that corresponds to the pressure or activity a_g of the volatile compound.

Chemical Potentials and Standard States for Completely Ionized Solutions

Complementary to the above we here specify the chemical potential for component i that has completely ionized in solution according to the scheme $M_{\nu+}A_{\nu-} = \nu_+M^{z+} + \nu_-A^{z-}$ for use in Eq. (4.1.6b). Consider now a saturated solution of a solid (say, NaCl) dissolved in the solvent (such as water), for which $\Gamma_{i\pm}$ is replaced by $\Gamma_{i\pm}^s$, and $x_{i\pm}$, by $x_{i\pm}^s$. This solution is in equilibrium with pure solid (NaCl) whose chemical potential is given by

$$\mu_i(T, P) = \mu_i^*(T, 1) + RT \ln \Gamma_i(T, P). \quad (4.1.12)$$

For all but the most accurate determinations we may neglect the above logarithmic term. We then find that Eq. (4.1.4) becomes

$$\mu_i(T, P, x_{i\pm}^s) - \mu_i^*(T, P) = \nu_i RT \ln [\Gamma_{i\pm}^s(T, P, x_{i\pm}^s) x_{i\pm}^s]. \quad (4.1.13)$$

The second term on the left hand side represents the molar free energy change of formation of the solid from its elements; hence, the left is equivalent to the free energy of formation of the solid in the saturated solution; we therefore write

$$\Delta \tilde{G}_{f,T}^{0,s} = \nu_i RT \ln [\Gamma_{i\pm}^s(T, P, x_{i\pm}^s) x_{i\pm}^s]. \quad (4.1.14)$$

From the above one can obtain $\Delta \tilde{H}_{f,T}^{0,s}$ and $\tilde{S}_{f,T}^{0,s}$ by standard differentiation with respect to T .

Activities of Volatile Components

As a prototype we consider a solution generated from dissolved HCl (aq) in equilibrium with HCl (g) in the gas phase. When taking into account that these species are in chemical equilibrium and that the ionic species H^+ and Cl^- predominate in solution we find that

$$\mu_{HCl}^{OP}(T) + RT \ln [f_{HCl}] = \mu_{HCl}^*(T, P) + 2RT \ln [\Gamma_{\pm}(T, P, x_{\pm}) x_{\pm}]. \quad (4.1.15)$$

In the above we collect all variable terms on the left and the remainder, on the right, to obtain in an obvious notation

$$RT \ln [f_{HCl} / \Gamma_{\pm}^2(T, P, x_{\pm}) x_{\pm}^2] = RT \ln K. \quad (4.1.16)$$

Since K is fixed for a given T and P one can in principle² determine K by working with solutions at sufficiently low mole fractions where the activity coefficient is sensibly unity. Having found K one can then operate at mole fractions for which $\Gamma_{\pm}(T, P, x_{\pm})$ is to be found.

Standard States for Electrolyte Solutions

As already mentioned, it is not possible to measure the thermodynamic properties of single ions. Nevertheless, it would be highly desirable to set up such a compilation, so that an experimentalist does not have to measure the literally thousands of cationic–anionic combinations whose properties are of interest. Since the thermodynamic characteristics of such pairings are algebraically additive one is at liberty to set up the following convention:

At any temperature the standard state of H^+ in aqueous form is taken to be zero.

That is, we set $\Delta\tilde{G}_{f,T}^0(\text{H}^+, \text{aq}) = 0$. Then the thermodynamic properties of anions can be found by measuring the chemical potentials of ionic solutions containing H^+ (as, for example, by the technique of galvanic cell electromotive forces (emfs), described below) in combination with different anions, and then using Eq. (4.1.3b). The anionic chemical potentials so determined can be employed as secondary standards in solutions containing different cations, and this matching process is continued as needed. Extensive tabulations constructed in this manner are available. However, this convention becomes inapplicable for processes where H^+ ions are transported across the phase boundaries of the aqueous solutions.

Since the entropy of H^+ ions is found via the temperature derivative of the Gibbs free energy of its formation, and the latter is independent of T by the above convention, one obtains $\Delta\tilde{H}_{f,T}^0(\text{H}^+, \text{aq}) = \tilde{S}_{f,T}^0(\text{H}^+, \text{aq}) = 0$, in consonance with the fact that $\Delta\tilde{G}_{f,T}^0(\text{H}^+, \text{aq}) = 0$.

Exercise and Comment

- 4.1.1. Adapt the above relations so as to apply to the use of molalities rather than mole fractions.
 4.1.2. Strictly speaking, one should add an inert gas in variable amounts sufficient to keep the total pressure P at a constant value during all the measurements. Alternatively, one may employ a piston.

4.2 Theoretical Determination of Activities in Electrolyte Solutions; the Debye–Hückel Equation

Having dealt with activities and activity coefficients in solutions made up from strong electrolytes, we now turn to the determination of Γ_{\pm} in weak electrolytic solutions. For this purpose we discuss some applications of the *Debye–Hückel theory*.

Ionic Strength

We first call attention to the concept of *ionic strength* introduced by Lewis and Randall in 1921. This quantity is defined as

$$S_i = (1/2) \sum_j m_j z_j^2, \quad (4.2.1)$$

in which m_j ($\equiv m_+$ or m_- for every ion j) is the molality of the j th ionic species in solution and z_j is the formal valence on the corresponding ion. The summation is to be carried out over *all* ionic species present in solution, *not* just over the species of interest. This definition corresponds to the experimental fact that in dilute solutions the activity coefficient of any electrolyte is the same in all solutions of the same ionic strength, regardless of the chemical nature of the dissolved ions.

The Debye–Hückel Equation

The treatment of dilute electrolytes is based principally on the theory developed by Debye and Hückel (1923), which is taken up in Section 9.5. As stated earlier, this somewhat lengthy treatment transcends

the methodology of classical thermodynamics and is presented separately, so as not to distract from the strictly thermodynamic approach presented below.

The *Debye–Hückel limiting law* specifies the following relations: For the individual ionic species, the activity coefficient in Section 9.5 is given by

$$\ln \Gamma_+ = -z_+^2 C_\ell \sqrt{S_i} / (1 + C_2 \sqrt{S_i}) \quad (4.2.2a)$$

$$\ln \Gamma_- = -z_-^2 C_\ell \sqrt{S_i} / (1 + C_2 \sqrt{S_i}), \quad (4.2.2b)$$

whereas the mean molar activity coefficient, which is the experimentally observable quantity, is specified as

$$\ln \Gamma_\pm = -f \frac{z_+ |z_-| C_\ell \sqrt{S_i}}{1 + C_2 \sqrt{S_i}}, \quad (4.2.3a)$$

where, Eq. (9.5.17), $f \equiv (\nu_+ z_+^2 + \nu_- z_-^2) / \nu$; $\nu = \nu_+ + \nu_-$. The ν s are stoichiometric coefficients, and z_i represents the valence of the ionic species. Here Γ_\pm represents the mean activity coefficient, which, as usually cited is taken with respect to molarity as the concentration unit (see below). According to the derivations of Section 9.5, the coefficients in Eq. (4.2.3a) are specified by

$$C_\ell \equiv \frac{1}{4\pi\sqrt{2000}} \cdot \frac{N^2 e^3}{(\epsilon_0 \epsilon R T)^{3/2}} = \frac{e^3 N^2}{(\epsilon R T)^{3/2}} \left(\frac{2\pi}{1000} \right)^{1/2}, \quad (4.2.3b)$$

where the intermediate formulation is appropriate for International System of Units and molarity, and the second, for centimeter–gram–second units and molarity.¹ Similarly,

$$C_2 \equiv \left(\frac{2N^2 e^2 \bar{a}^2}{1000 \epsilon_0 \epsilon R T} \right)^{1/2} = \left(\frac{8\pi e^2 \bar{a}^2 N^2}{1000 \epsilon R T} \right)^{1/2}. \quad (4.2.3c)$$

In the above $-e$ is the electronic charge, \bar{a} the average ionic diameter, N Avogadro's number¹, ϵ the dielectric constant, ϵ_0 the permittivity of vacuum, and R the gas constant, Generally, $C_2 \sqrt{S_i}$ is small relative to unity; one then deals with the *extreme limiting law*:

$$\ln \Gamma_\pm = -z_+ |z_-| C_\ell \sqrt{S_i}. \quad (4.2.3d)$$

On switching from natural to common logarithms and inserting numerical values for C_ℓ and C_2 one obtains the following result, valid for aqueous solutions at room temperature:

$$\log \Gamma_\pm = -f \frac{0.5092 z_+ |z_-| \sqrt{S_i}}{1 + \sqrt{S_i}} \quad (T = 298.16 \text{ K}), \quad (4.2.4)$$

where \bar{a} in Eq. (4.2.3c) has been set at 0.31 nm. As already noted in conjunction with Eq. (4.2.3d), the denominator is ordinarily replaced by unity, under conditions where the theory is applicable $\sqrt{S_i} \ll 1$. If the constants C_ℓ and C_2 are to be computed at other temperatures one must take into account not only the $T^{-3/2}$ factor in Eq. (4.2.3b) but also the variation of ϵ with T , which is substantial for water.

One should note the following: (i) Eq. (4.2.4) applies to any aqueous electrolyte solution at room temperature, but (ii) with limits of applicability generally restricted to solutions of molality 10^{-2} or less.² (iii) The activity coefficients for different solutions of the same ionic strength and for the same ionic valence are the same. (iv) A plot of $\log \Gamma_{\pm}$ vs $\sqrt{S_i}$ for extremely dilute solutions should yield a straight line of limiting slope $-0.5092 z_+ |z_-|$ in aqueous solution at room temperature. Extensive testing over a long period of time has confirmed the correctness of this prediction. (v) It has been verified by use of different solvents in the limiting case of dilute solutions that $-\log \gamma_{\pm} \sim \epsilon^{-3/2}$.

In the current discussion, the mean activity coefficient is related to molarity. On the other hand, the definition of ionic strength involves molality as the basic concentration variable. However, as is to be proved in Exercise 4.2.3, for aqueous solutions at ordinary temperatures and pressures the definition of S_i remains virtually unaltered by switching from molarity to molality. Thus, the quantity specified by Eq. (4.2.3a) may be considered to represent either $\Gamma_{\pm}(T, P, c) \equiv \Gamma_{\pm}^{(c)}$ or $\Gamma_{\pm}(T, P, m) \equiv \Gamma_{\pm}^{(m)}$. However, for very precise work, or when nonaqueous solvents are employed, or whenever T and P deviate greatly from standard conditions (SC), the two preceding quantities cannot be used interchangeably; Eq. (4.2.3a) specifies $\Gamma_{\pm}^{(m)}$ and Eqs. (4.2.3b) and (4.2.3c) must be suitably modified.

As has already been stressed, the Debye–Hückel relation, even in the form (4.2.3a), is of only limited applicability. In attempts to extend the range over which it remains useful one of the most widely used versions reads

$$\ln \Gamma_{\pm}^{(m)} = -f \frac{z_+ |z_-| C_{\ell} \sqrt{S_i}}{1 + C_2 \sqrt{S_i}} + \frac{2\nu_+ \nu_-}{\nu} C_2 m_{\pm}, \quad \nu = \nu_+ + \nu_-, \quad (4.2.5)$$

in which C_3 is a purely empirical constant whose value must be determined by experiment. Equation (4.2.5) is sometimes termed the *extended Debye–Hückel equation*.

Comment and Exercises

- 4.2.1** The presence of Avogadro's number causes problems. One factor of N arises in the derivation of Section 9.5 since we took $\mu = \mu_0 + k_B T \ln(c\Gamma)$ to be the chemical potential per ion. The factor would be missing in the per mole specification. A second factor of $N^{1/2}$ arises from specifying the definition of κ^2 , Eq. (9.5.5d), in terms of R rather than k_B . A final factor of $N^{1/2}/\sqrt{1000}$ arises when converting $S^{1/2}$ from number of ions per cubic meter to number of moles/l. An additional factor of 2.303 is needed in the denominators to convert from natural to ordinary logarithms.
- 4.2.2** It is sometimes asserted that the Debye–Hückel limiting law applies only to slightly contaminated distilled water.
- 4.2.3** Show that there is very little difference in the results derived in the present section for aqueous solutions when molality is replaced by molarity. Why is this not the case for nonaqueous solvents?
- 4.2.4** Suggest a method for rewriting the Debye–Hückel equation so that one may easily determine the value of a for the effective ionic diameter, which may also be viewed as the average distance of closest approach between ions.

Experimental Determination of Activities and Activity Coefficients of Strong Electrolytes

Since the Debye–Hückel method is limited to very dilute solutions, experimental methods must be invoked to find Γ_{\pm} for $m > 10^{-2}$ molal. The derivations are largely patterned after Section 2.8. The use of emf methods for the same purpose is briefly dealt with below Eq. (4.7.2). Once again, the choice of $P = 1$ bar serves as the standard pressure; in this case the activity coefficient Γ_i introduced in Section 3.3 is appropriate. When molalities are used as concentration units the expression $\Gamma_{\pm}^{(m)}$ serves the purpose.

Vapor Pressure Measurements

Vapor pressure measurements may be used to determine the activity of the solvent. Equation (3.6.4) may be taken over without change:

$$\Gamma_1^{(x)} \approx P_1/P_1^* x_1, \quad (4.2.6)$$

where P_1^* is the vapor pressure of pure solvent and P_1 is the vapor pressure of the solvent in the presence of the electrolyte.

Use of Gibbs–Duhem Equation

The Gibbs–Duhem relation (1.14.13) may be used in conjunction with the foregoing to determine the molar activity of the ionic species in a binary solution. This is necessary because a direct determination is difficult. The subsequent relations are generally couched in terms of molalities. We proceed as follows: since $d \ln a_2^{(x)} = d \ln a_2^{(m)}$, we use the form (T and P constant; for the solvent, $m_1 = 1000/M_1$)

$$\frac{1000}{M_1} d \ln a_1^{(x)} + m_2 d \ln a_2^{(m)} = 0, \quad (4.2.7a)$$

wherein

$$a_2^{(m)} \equiv \left(a_2^{(m)}\right)_{\pm}^{\frac{1}{2}}; \quad m_2^{(m)} \equiv \left(m_2^{(m)}\right)_{\pm}^{\frac{1}{2}}, \quad \nu_{2+} + \nu_{2-} \equiv \nu_2. \quad (4.2.7b)$$

Integration coupled with the use of (3.6.4), yields

$$\int_{m_l}^{m_u} d \ln a_2^{(m)} = - \int_{m_l}^{m_u} \frac{1000}{M_1 m_2} d \ln a_1^{(x)} \approx - \int_{m_l}^{m_u} \frac{1000}{M_1 m_2} d \ln \frac{P_1}{P_1^*}. \quad (4.2.8)$$

Thus, plots of $1000/M_1 m_2$ vs $\ln(P_1/P_1^*)$ yield a value of the integral on the right for molalities between the lower and upper limits $m_l \leq m_2 \leq m_u$; the left hand is given by $\ln[a_2(T, 1, m_u)/a_2(T, 1, m_l)]$. The problem with this approach is that changes in the vapor pressure cannot be measured with sufficient accuracy in very dilute solution. One must therefore employ this procedure in conjunction with the Debye–Hückel limiting law, which holds for $m_2 < m_l \approx 10^{-2}$.

Freezing Point Depression Measurements

Freezing point depression measurements furnish another convenient approach to determine the activity of the *solvent*. Equation (2.8.7) or the subsequent simplified versions may be taken over without change because we have not had occasion to refer to the ionic dissociation process.

For the determination of the activity of the ionic solute in a binary solution we modify Eq. (3.7.9) by writing ($m_2 \equiv m$; $\nu \equiv \nu_+ + \nu_-$ for the compound $M_{\nu_+}A_{\nu_-}$)

$$d \ln a_{\pm}^{(m)} = \left(\frac{1}{\nu}\right) d \ln a_2^{(m)} = \frac{d\Theta}{\nu\lambda m} + \frac{c\Theta}{\nu m} d\Theta. \quad (4.2.9)$$

and in place of (3.7.10) we introduce

$$j \equiv 1 - \Theta/\nu\lambda m. \quad (4.2.10)$$

It should be verified that Eq. (3.7.11b) is replaced by

$$d\Theta/\nu\lambda m = (1-j)d \ln m - dj. \quad (4.2.11)$$

Next, set $a^{1/\nu} = a_{\pm}$, $m_+ = \nu_+ m_+$, $m_- = \nu_- m_-$, so that $m_{\pm} = m(\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu}$. It follows that

$$d \ln \Gamma_{\pm}^{(m)} = d \ln \left\{ \frac{a_{\pm}^{(m)}}{m(\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu}} \right\} = d \ln \left(\frac{a_{\pm}^{(m)}}{m_{\pm}} \right) \equiv d \ln \left(\frac{a_{\pm}^{(m)}}{m} \right). \quad (4.2.12)$$

Thus, in place of (3.7.12) we find from Eqs. (4.2.9–4.2.12),

$$d \ln \Gamma_{\pm}^{(m)} = d \ln a_{\pm}^{(m)} - d \ln m = -jd \ln m - dj + \frac{c\Theta}{\nu m} d\Theta, \quad (4.2.13)$$

whose integration yields the analog of (3.7.13), namely,

$$d \ln \Gamma_{\pm}^{(m)}(T_f) = -j - \int_0^m \left(\frac{j}{m}\right) dm + \left(\frac{c}{\nu}\right) \int_0^m \left(\frac{\Theta}{m}\right) d\Theta. \quad (4.2.14)$$

We now replace the central term by its equivalent formulation $2 \int_0^m (j/m^{1/2}) dm^{1/2}$, since for strong electrolytes $j/m^{1/2}$ remains finite as $m \rightarrow 0$. Finally, you need to check that at any temperature other than T_f one obtains

$$\ln \Gamma_{\pm}^{(m)}(T) = \ln \Gamma_{\pm}^{(m)}(T_f) - \left(\frac{b_1}{\nu}\right) \int_0^m \frac{1}{m} dy, \quad (4.2.15)$$

in which $b_1 \equiv 1000/M_1$.

Solubility Measurements

Frequently, solubility measurements may be used in mixed electrolytes to obtain mean molar activity coefficients. This method hinges on the use of an electrolyte solution that is saturated with respect to any particular salt, so that the equilibrium $M_{\nu_+}A_{\nu_-}(s) = \nu_+ M^{z_+} + \nu_- A^{z_-}$ prevails. This situation may be characterized by (among others) use of the equilibrium constant. It is conventional either to ignore

the product term $[a_{is}^*(T, P)]^\nu$ as being equal to (at unit pressure) or close to unity, or to absorb this constant factor into the equilibrium constant as well. This then gives rise to the expression

$$K_m'' = \frac{a_+^{\nu+} a_-^{\nu-}}{a_{M_{\nu+}A_{\nu-}}}. \quad (4.2.16a)$$

Since the activity of pure $M_{\nu+}A_{\nu-}$ is a constant, it, too, may be absorbed into the equilibrium constant; this step finally yields

$$K_s = a_+^{\nu+} a_-^{\nu-} = a_{\pm}^{\nu} = (m_{\pm} \Gamma_{\pm})^{\nu}. \quad (4.2.16b)$$

Inversion of this relation leads to

$$\Gamma_{\pm}^{(m)} = \frac{K_s^{1/\nu}}{m_{\pm}}. \quad (4.2.17)$$

The procedure now consists in adding other strong electrolytes to the solution. Since K_s remains unaffected by this step while $\Gamma_{\pm}^{(m)}$ of the electrolyte of interest necessarily changes, m_{\pm} will change in the opposite direction. One thus measures m_{\pm} from the observed solubilities of the salt $M_{\nu+}A_{\nu-}$ in the presence of other salts added in varying amounts. The results may then be extrapolated to infinite dilution on a plot of m_{\pm} vs $\sqrt{S_i}$, where S_i is the ionic strength defined in Eq. (4.2.1). This permits an extrapolation to zero molality where $\Gamma_{\pm}^{(m)} = 1$. The mean molality obtained from this extrapolation thus yields $K_s^{1/\nu}$. Measuring m_{\pm} for any other value of S_i then yields the desired $\Gamma_{\pm}^{(m)}$.

Two additional observations: first, the methods used here treat each of the ionic types as a separate species that influences the thermodynamic properties of solutions very strongly by virtue of its associated charge. Second, it is instructive to examine the dependence of the mean molal activity coefficient for several different electrolytes as a function of the molality. Representative examples are shown in Figure 4.2.1. One sees at first a very steep drop in Γ_{\pm} as m is increased, and then either a gradual or a very sharp rise in Γ_{\pm} as m is increased beyond 0.5. The greater the value $z_+|z_-|$ the sharper is the initial drop-off. [Explain why.]

Equilibrium Properties of Weak Electrolytes

General Discussion

The Debye–Hückel equation works well for very dilute solutions, but empirical methods are necessary to deal with even weak electrolytes at ordinary concentrations. Weak electrolytes involve the equilibration of undissociated $M_{\nu+}A_{\nu-}$ with its ions in solution according to the schematic reaction $M_{\nu+}A_{\nu-} = \nu_+ M^{z+} + \nu_- A^{z-}$. There are many different ways of characterizing equilibrium conditions. Here we shall adopt Eq. (3.4.11) for the equilibrium constant; when $M_{\nu+}A_{\nu-}$ represents a pure phase we find

$$K'_x = \frac{a_+^{\nu+} a_-^{\nu-}}{a_{M_{\nu+}A_{\nu-}}}. \quad (4.2.18)$$

According to the adopted standard states, the activity of undissociated $M_{\nu+}A_{\nu-}$ in the pure condensed state is equal to unity. If the pressure does not deviate significantly different from SC, a does not

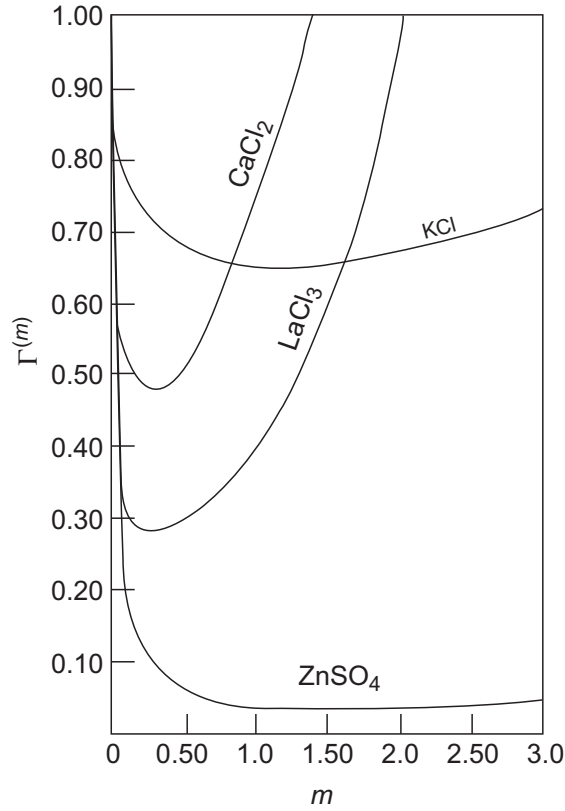


FIGURE 4.2.1

Variation of mean molal activity coefficients as a function of molality for several salts dissolved in aqueous solutions.

deviate significantly from unity. In either case, this factor may then be dropped, so that the equilibrium constant now reads

$$K_x = (a_+^{\nu+} a_-^{\nu-}) = (a_{\pm})_{eq}^{\nu}. \quad (4.2.19)$$

Equation (4.2.19) may be rewritten in terms of activity coefficients as

$$K_q = [x_{\pm} \Gamma_{\pm}(T, P, x_{\pm})]_{eq}^{\nu}, \quad (4.2.20)$$

K_q is termed the *solubility product constant*: under standard conditions (SC),

$$K_s = [x_{\pm} \Gamma_{\pm}(T, 1, x_{\pm})]_{eq}^{\nu}. \quad (4.2.21)$$

If, on the other hand, $M_{\nu+}A_{\nu-}$ represents a dissolved but unionized species one then deals with the partial dissociation of a weak electrolyte, which then involves an equilibrium constant in the form

$$K_x'' = \frac{\prod_i (x_{i+} \Gamma_{i+})_{eq}^{\nu_{i+}} \prod_j (x_{j-} \Gamma_{j-})_{eq}^{\nu_{j-}}}{(x_0 \Gamma_0)_{eq}^{\nu_0}} = \frac{\prod_i [x_{i\pm} \Gamma_{i\pm}(T, 1, x_{i\pm})]_{eq}^{\nu}}{(x_0 \Gamma_0)_{eq}^{\nu_0}}, \quad (4.2.22)$$

in which the subscript zero refers to the undissociated species; since the latter is electrically neutral, deviations from ideality are often neglected by setting $\Gamma_0 = 1$.

Examples

In what follows, general principles are illustrated by specific examples.

- (a) The case of water is well known: here one deals with the equilibrium $\text{H}_2\text{O}(\ell) = \text{H}^+ + \text{OH}^-$, which leads to the equilibrium constant

$$K_w = a_{\text{H}^+} a_{\text{OH}^-} / a_{\text{H}_2\text{O}}. \quad (4.2.23)$$

It is customary to take $a_{\text{H}_2\text{O}} = 1$, which is strictly correct only if $P = 1$ bar and if no other dissolved species are present.

K_w has been measured carefully as function of temperature over a considerable temperature interval; for each temperature K_w may be determined from conductivity or from emf measurements, the latter technique being described in Section 4.8. The heat of ionization per unit advancement of the ionization reaction may be determined according to Eq. (2.10.3a) in conjunction with van't Hoff's law. This requires knowledge of how Γ_{\pm} changes with T . Details, based on Section 3.7, are to be handled in Exercise 4.2.5, which you should work out in detail.

- (b) Another elementary case of interest involves the ionization of acetic acid (HA), which is representative of a whole class of materials that dissociate only weakly. Here one deals with the equilibrium $\text{HA} = \text{H}^+ + \text{A}^-$, which is characterized by the equilibrium constant

$$K_A = \frac{a_{\text{H}^+} a_{\text{A}^-}}{a_{\text{HA}}} = \frac{\Gamma_{\text{H}^+} c_{\text{H}^+} \Gamma_{\text{A}^-} c_{\text{A}^-}}{\Gamma_{\text{HA}} c_{\text{HA}}}, \quad (4.2.24)$$

where A^- represents the acetate ion. Strictly speaking, one should account for the water dissociation equilibrium, which provides the common ion H^+ , but this contribution is usually negligible compared to the H^+ ion concentration generated via the dissociation of HA. Since HA is neutral no significant error is made in setting $\Gamma_{\text{HA}} = 1$. If we write $\Gamma_{\pm} = (\Gamma_{\text{H}^+} \Gamma_{\text{A}^-})^{1/2}$ we obtain from Eq. (4.2.24)

$$\log \frac{c_{\text{H}^+} c_{\text{A}^-}}{c_{\text{HA}}} = \log K_A - 2 \log \Gamma_{\pm}, \quad (4.2.25)$$

and on using the Debye–Hückel Eq. (4.2.3a), we obtain the result

$$\log \frac{c_{\text{H}^+} c_{\text{A}^-}}{c_{\text{HA}}} = \log K_A + \frac{2(2.303)C_{\ell}\sqrt{S_i}}{1 + C_2\sqrt{S_i}}. \quad (4.2.26)$$

Next, introduce the degree of dissociation, α ; then $c_{\text{H}^+} = c_{\text{A}^-} = \alpha c = c_{\text{HA}} = (1 - \alpha)c$, c being the starting concentration. We now find

$$\log \frac{c\alpha^2}{1 - \alpha} = \log K_A + \frac{2(2.303)C_{\ell}\sqrt{c\alpha}}{1 + C_2\sqrt{c\alpha}}, \quad (4.2.27)$$

in both of which $C_2 \approx 1$ at room temperature. Equation (4.2.26) involves the ionic strength and is applicable if the solution contains other strong electrolytes with no ions in common with H^+ or A^- . Equations (4.2.26) and (4.2.27) show the extent to which the quantity $\frac{c_{\text{H}^+} c_{\text{A}^-}}{c_{\text{HA}}}$ differs from K_A .

- (c) We turn next to hydrolysis reactions, typified by the interaction with water of the salt BA formed from a strong base BOH and a weak acid HA: $A^- + H_2O \rightarrow HA + OH^-$. Here it is implied that a compensating cation such as Na^+ is present, so as to maintain electroneutrality. Correspondingly, if one ignores the common ion effects arising from the ionization of water we obtain

$$K_H = \frac{a_{OH^-} a_{HA}}{a_{A^-} a_{H_2O}} = \frac{a_{\pm NaOH}^2 a_{HA}}{a_{\pm NaA}^2 a_{H_2O}}. \quad (4.2.28)$$

If again we set $a_{H_2O} = 1$ and $a_{HA} = c a_{HA}$,

$$K_H = \frac{(\Gamma_{\pm NaOH})^2 (c_{\pm NaOH})^2 (c_{HA})}{(\Gamma_{\pm NaA})^2 (c_{\pm NaA})^2}. \quad (4.2.29)$$

If BA is the salt of a weak base and strong acid the relevant hydrolysis reaction reads $B^+ + H_2O = BOH + H^+$, which in the presence of a compensating concentration of Cl^- ions (assuming that BCl is not present in undissociated form and that the common ion effects arising from the dissociation of water can be ignored) leads to the expression

$$K_H = \frac{a_{B^+} a_{H_2O}}{a_{H^+} a_{BOH}} = \frac{a_{\pm HCl}^2 a_{BOH}}{a_{\pm BCl}^2 a_{H_2O}}. \quad (4.2.30)$$

If BA is the salt of a weak base BOH and a weak acid HA, the relevant reaction is written as $B^+ + A^- + H_2O = BOH + HA$. Here it has been assumed that BA dissociates completely. Then the equilibrium constant assumes the following form:

$$K_H = \frac{a_{BOH} a_{HA}}{a_{\pm BA}^2 a_{H_2O}}. \quad (4.2.31)$$

- (d) Next, we turn briefly to the case in which a pure solid A(s) is in equilibrium with undissociated A in solution, which in turn is in equilibrium with A_+ and A_- according to the schematic equation $A(s) = A = \nu_+ A_+ + \nu_- A_-$. The equilibrium situation is characterized by

$$\mu_S = \mu_A = \nu_+ \mu_+ + \nu_- \mu_-. \quad (4.2.32)$$

In the event there is no undissociated A, we obtain the relation

$$a_+^{\nu_+} a_-^{\nu_-} = K, \quad (4.2.33)$$

where K is termed the *activity product*, which may be compared with three solubility products:

$$L_x = x_+^{\nu_+} x_-^{\nu_-}, \quad L_c = c_+^{\nu_+} c_-^{\nu_-}, \quad L_m = m_+^{\nu_+} m_-^{\nu_-}. \quad (4.2.34)$$

Thus, in each case one obtains an interrelation of the type

$$K^{1/\nu} = L^{1/\nu} \Gamma_{\pm}. \quad (4.2.35)$$

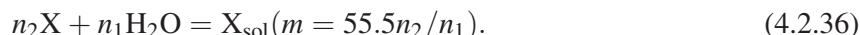
Thermochemistry of Solutions

Properties of ionic solutions are described in a unified manner by introducing a convention:

The enthalpy of a pure liquid solvent at temperature T and at pressure P (ordinarily, 1 bar) is set equal to zero, unless the solvent participates in a chemical reaction with the solute, in which case the usual chemical conventions are applied to specify the enthalpy of interaction.

The convention enables us to ignore the enthalpies of formation of inert solvents, which, in any event, cancel out in establishing the energetics of reactions executed in solutions.

As an example consider the dissolution of n_2 moles of solute (X) in n_1 moles of water, whose “molality” as pure solvent is $m = 55.5$. We write out the “reaction” as



Experimentally it is reported that for $n_2 = 1$ mol HCl gas dissolved in $n_1 = 10$ mol of H_2O at 298.15 K under a pressure of 1 bar $\Delta H_{\text{sol}}^0(m = 5.55) = -69.3$ kJ/mol HCl, which quantity is known as the *integral heat (enthalpy) of solution*. When added to the standard enthalpy of formation, $\Delta H_f^0 = -92.1$ kJ/mol HCl, one obtains $\Delta H_f(m = 5.55) = -161.4$ kJ/mol HCl. On adding another 10 mol H_2O the resulting *integral heat of dilution* is found to be $\Delta H_{\text{dil}} = -2.5$ kJ/mol HCl, so that the total integral enthalpy of solution is given by $\Delta H_{\text{sol}}^0(m = 2.78) = -761.8$ kJ/mol HCl. This represents an example of the diminishing rate of increase of the heats of dilution with diminishing solute concentration. In general a curve such as shown in Figure 4.2.2 is encountered; one notes that as infinite dilution is approached the integral enthalpy of solution approaches a constant value. These facts call for the definition of a *differential enthalpy of solution*, given by

$$\Delta \bar{H}_i = (\partial \Delta H_{\text{sol}} / \partial n_i)_{T, P, n_{i \neq j}}, \quad (4.2.37)$$

which is simply the slope of the curve in Figure 4.2.2.

When two infinitely dilute solutions containing ions are mixed without reacting there is essentially no enthalpy of mixing for this process. However, if an interaction does occur, such that a precipitate or more solvent, of some other compound, is formed, a chemical reaction has occurred that is characterized by an enthalpy change for that process. In sufficiently dilute solution these enthalpy changes depend only on the ions that are involved in the process and not on the partner ions that remain behind. It then becomes possible to adopt another simplifying convention:

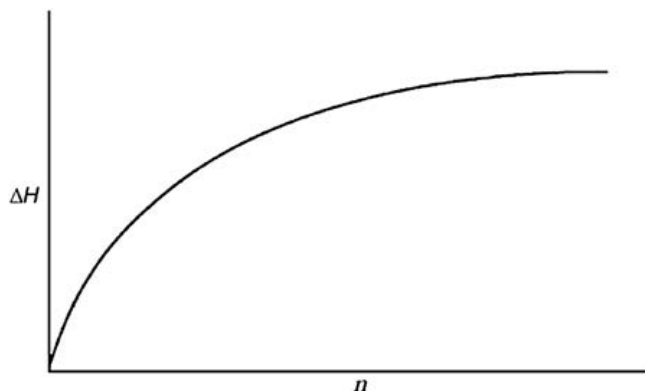


FIGURE 4.2.2

Schematic diagram for heats of solution when n moles of solvent are added to one mole of solute.

The enthalpy of formation of H^+ ions in an infinitely dilute solution of water, ΔH_f^∞ , is set at zero at all temperatures and pressures.

This convention enables us to assign ΔH_f^∞ values to other ions: for example, by measuring the enthalpy for forming an infinitely dilute solution of HCl (the limiting value of the curve in Figure 4.2.2) as $\Delta H_{\text{sol}}^\infty = -75.1 \text{ kJ/mol HCl}$, and adding this to the standard enthalpy of formation of HCl, $\Delta H_f^0(\text{HCl, g}) = -92.1 \text{ kJ/mol}$, the enthalpy of formation of Cl^- in water at infinite dilution is then given by $\Delta H_f^\infty(\text{Cl}^-) = -167.4 \text{ kJ/mol}$. A whole set of values for various anionic species can be similarly constructed, and these, in turn, may be used as secondary standards to be paired off with different cations for ΔH_f^∞ measurements.

Once these quantities are known one can readily construct enthalpies of interaction such as the precipitation of AgCl from H^+ and Cl^- : $\Delta H_f^\infty(\text{AgCl}) = \Delta H_f^\infty(\text{Ag}^+) + \Delta H_f^\infty(\text{Cl}^-)$. As another example, one may determine the enthalpy of formation of the compound NaCl at infinite dilution from $\Delta H_f^\infty(\text{NaCl}) = \Delta H_f^\infty(\text{Na}^+) + \Delta H_f^\infty(\text{Cl}^-)$; this value may be checked against the determination obtained from $\Delta H_f^\infty(\text{NaCl}) = \Delta H_f^0(\text{NaCl, s}) + \Delta H_{\text{sol}}^\infty(\text{NaCl})$. However, such calculations are of rather limited usefulness since processes of interest normally involve ions at finite concentrations whose properties change in the course of the interaction. These determinations are also affected by the presence of nonparticipating ions in solution, so that the machinery developed earlier and set forth later is needed to handle such a situation.

Entropies and Free Energies of Ionic Species

Very similar conventions may be introduced to characterize the entropies and Gibbs free energies of ionic species. Here one adopts the convention that at $T = 298.15 \text{ K}$ and at 1 bar $\tilde{S}^0(\text{H}^+) = 0$ and $\Delta \tilde{G}_f^0(\text{H}^+) = 0$, for water as solvent. Tabulations of molar entropies and free energies may then be constructed as outlined earlier. These are also of the same rather limited applicability as the comparable enthalpies for ions. As an example, one may determine the equilibrium constant for a given ionic reaction at infinite dilution through the relation, $\Delta G_f^0 = -RT \ln K_{\text{ion}}$, for which the left hand side is first established by looking up the relevant data from the tabulations.

Exercise

4.2.5. Consult Section 3.7 so as to work out the details on the heat of ionization of water.

4.3 Galvanic Cells

General Description

In describing the operation of galvanic cells we introduce a specific example rather than invoking the cumbersome machinery needed for a generalized approach. The example chosen for this purpose can then easily be extended for a more general analysis of galvanic processes.

Consider then the operation of the Daniell cell depicted in Figure 4.3.1, which serves as a prototype. The two compartments are filled, respectively, with a saturated ZnSO_4 solution in contact with a Zn strip (left), and a saturated CuSO_4 solution in contact with a Cu strip (right). The two metallic electrodes are

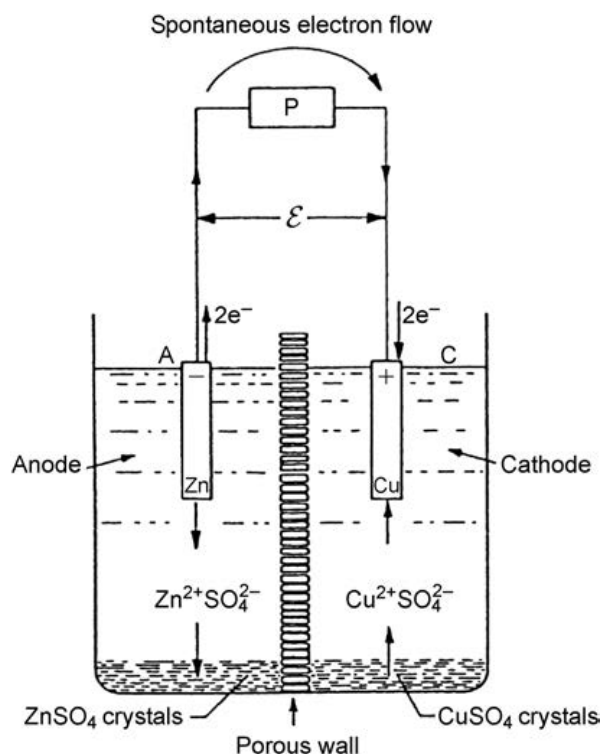


FIGURE 4.3.1

Schematic diagram of the Daniell cell. The rectangular box labeled P represents a potentiometer. Anode and cathode are shown for the spontaneous operation of the cell when the potentiometer emf is slightly less than that of the cell. Zn at the anode enters the solution as Zn^{++} ions and Cu^{++} in the cathode compartment deposits as Cu.

joined electrically to a variable potentiometer. A salt bridge that permits transfer of ionic species connects the two compartments. Electrochemical processes now ensue: the metallic electrodes interact with the ionic components according to the net reactions: $\text{Zn} = \text{Zn}^{2+} + 2\text{e}^-$, and $\text{Cu} = \text{Cu}^{2+} + 2\text{e}^-$.¹ One finds that the tendency of Zn to go into solution, thereby furnishing electrons to the metallic wire, is stronger than the opposing tendency of Cu to do the same. Accordingly, in the spontaneous operation of the cell, the second reaction is reversed as $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$. The combination of these two processes allows electrons to be transferred from left to right through the external circuit shown in Figure 4.3.1. This natural process can be arrested by setting up an opposing voltage in the potentiometer, thereby establishing equilibrium conditions.¹ The electron flow may actually be reversed by increasing the opposing potentiometer voltage, thus forcing the electrons to flow from right to left, with corresponding reversals in the indicated electrochemical reactions. By minor adjustment of potentiometer settings one can thus allow the cell to operate reversibly in either direction; thereby, electrochemical processes in the cell become amenable to thermodynamic analysis.²

Conventionally, a reaction such as $\text{Zn} = \text{Zn}^{2+} + 2\text{e}^-$ that furnishes electrons to the circuit (increasing the valence of Zn) is said to be an *oxidation* step, and the electrode where this occurs is called the *anode*. A reaction such as $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$ that removes electron from the external circuit (decreasing the valence of Cu^{2+}) is termed a *reduction* step, which occurs at the *cathode*. In the

spontaneous operation of the cell the Zn^{2+} ions furnished during oxidation of the metallic Zn strip accumulate in the saturated solution on the left and combine with available SO_4^{2-} ions to precipitate out ZnSO_4 . The Cu^{2+} ions, concomitantly removed from solution on the right, deposit on the metallic Cu strip and cause solid CuSO_4 to dissolve in a compensating process so as to replace the deposited Cu^{2+} ions. The resulting anionic imbalance in both compartments is compensated for by appropriate transfer of cations and anions into or out of the salt bridge, so as to maintain electroneutrality in both aqueous compartments. Obviously, all the above processes occur simultaneously. The net result is represented by the reaction $\text{Zn} + \text{CuSO}_4 = \text{Cu} + \text{ZnSO}_4$; however, the actual processes are clearly vastly more complex. Nevertheless, for the thermodynamic representation of the ongoing phenomena only the net reactions are needed. The resulting spontaneous current flow is thus a consequence of the chemical instability of Zn metal relative to a saturated solution containing Zn^{2+} ions; chemical potential energy has been transformed into electrical energy flow.

The above example illustrates the general characteristics of a galvanic cell. It usually consists of two ionic solutions (or, frequently, a solid material) often in separate but interconnected compartments, in physical contact with electrodes connected to a potentiometer; frequently, the electrodes are surrounded by reactive gases. Any departures from the quiescent conditions of open-circuit conditions are accompanied by oxidation–reduction processes that keep in step with the flow of electrons through the external circuit.

Remarks

- 4.3.1.** Strictly speaking, these are steady state, quiescent conditions, because the process is not allowed to run to completion as it would without imposition of external constraints, but we will ignore this distinction. In what follows it will always be assumed that any virtual changes away from quiescence are carried out reversibly, so that the system may be returned to the unchanged state without incurring any changes in the universe.
- 4.3.2.** Obviously, in everyday applications galvanic cells are operated in irreversible fashion during discharge and charge; thus, the voltages and operating conditions are not subject to the analysis provided in this chapter. Rather, the near steady state conditions considered here can only be used in a thermodynamic analysis of chemical processes detailed below.

4.4 Operation of Galvanic Cells

We next describe the operation of galvanic cells in mathematical terms, again taking the Daniell cell as our representative example. Consider Figure 4.4.1; when electrons flow through the external circuit left to right the *electric field* \mathcal{E} points in the direction of the conventional positive current flow, i.e., to the left, whereas the electrostatic potential gradient $\nabla\phi = -\mathcal{E}$ points to the right. Under spontaneous operating conditions involving the transfer of $1\mathcal{F}(\mathcal{F}; 1\mathcal{F} = 1 \text{ mol of electrons} = 96,495 \text{ C})$ in an infinite copy of the cell, the electron density, hence $\ln a_e$, rises ever so slightly from right to left. (Actually, under true steady state operations no gradient in electron density is encountered in the metallic wires.) Thus, electron flow is simultaneously affected by concentration gradients and by the

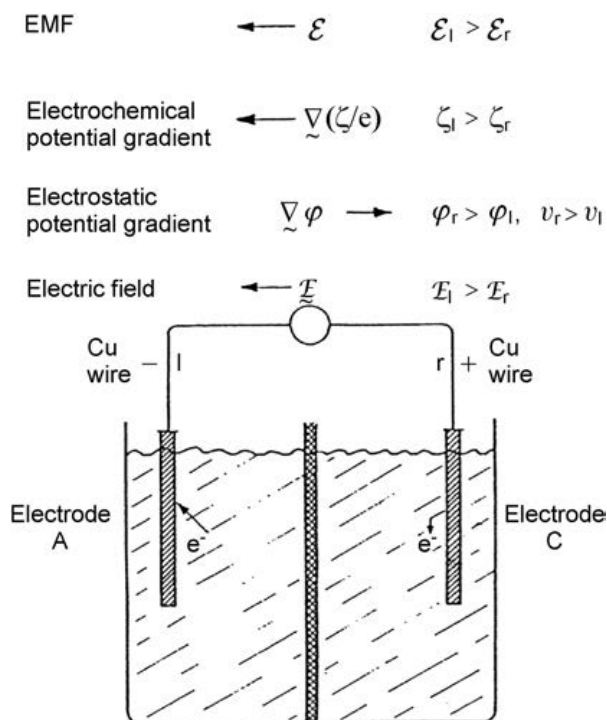
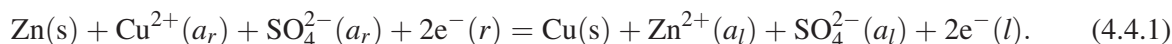


FIGURE 4.4.1

Schematic diagram showing the direction of the emf, electrochemical potential gradient, electrostatic potential gradient, and electric field during spontaneous operation of a cell operating in conformity with Conventions 1 and 2, described below.

externally applied electric field. To deal with this case it is apposite to introduce the concept of *electrochemical potential*, $\zeta \equiv \mu + z\mathcal{F}\phi$, with $z = -1$ for electrons, with a corresponding *electrochemical potential gradient* given by $\nabla\zeta = \nabla\mu - \nabla\mathcal{F}\phi = RT d \ln a_e - \nabla\mathcal{F}\phi$, which increases from right to left; $\zeta(l) > \zeta(r)$. It is this difference in the electrochemical potentials that drives the spontaneous electron transfer through the external circuit of the cell. A minimalist description of the above spontaneous operational process is then given by



Contrary to conventional practice, the electrons are included as part of the overall reaction: the electrochemical potentials at the two electrodes differ, being (at least partially) counteracted by the opposing voltage of the potentiometer. Therefore, the electron concentrations *do not cancel*. The solid species are indicated by (s), and the ionic activities in the two compartments, by the activity a . A detailed rationale for writing Eq. (4.4.1) as shown is provided as a footnote.¹

We next invoke the generalized equilibrium condition, $\sum_i \nu_i \zeta_i = 0 = \sum_i \nu_i (\mu_i + z_i \mathcal{F}\phi)$ where z_i is the charge on species i ; for uncharged species $\zeta_i = \mu_i$. As before, ζ_i and μ_i are the electrochemical and chemical potentials of species i in solution, ϕ is the electrostatic potential acting on the species, and the stoichiometric coefficients for reagents in the chemical reactions as written are negative. The equilibrium condition as applied to the Daniell cell operation reads²

$$\begin{aligned} & \mu_{\text{Zn(s)}}^* + \mu_{\text{CuSO}_4(\text{sol})}^* + RT \ln a_{\pm}^2(r) + 2\mathcal{F}\phi_{\text{Cu}^{2+}}(r) - 2\mathcal{F}\phi_{\text{SO}_4^{2-}}(r) + 2\mathcal{F}\zeta_e(r) \\ &= \mu_{\text{Cu(s)}}^* + \mu_{\text{ZnSO}_4(\text{sol})}^* + RT \ln a_{\pm}^2(l) + 2\mathcal{F}\phi_{\text{Zn}^{2+}}(l) - 2\mathcal{F}\phi_{\text{SO}_4^{2-}}(l) + 2\mathcal{F}\zeta_e(l). \end{aligned} \quad (4.4.2)$$

The subscript e refers to electrons. At equilibrium the positive and negative ions (the latter, after multiplication with -1) in solution in the left compartment are at the same electrostatic potential that preserves electroneutrality; similar reasoning applies to the ions in the right compartment. Hence, the terms involving ϕ cancel out. The terms $\mu_{\text{Zn(s)}}^* + \mu_{\text{CuSO}_4(\text{sol})}^* - \mu_{\text{Cu(s)}}^* - \mu_{\text{ZnSO}_4(\text{sol})}^*$ may be grouped into an equilibrium parameter, namely, $+RT \ln K_a$, as indicated in Section 3.4; (why the $+$ sign?). We can then solve Eq. (4.4.2) for

$$[2\mathcal{F}\zeta_e(l) - 2\mathcal{F}\zeta_e(r)] \equiv 2\mathcal{F}\mathcal{E} = RT \ln K_a = RT \ln \{a_{\pm}^2(l)/a_{\pm}^2(r)\}, \quad (4.4.3a)$$

where we have introduced the *emf* \mathcal{E} as³

$$\mathcal{E} \equiv [\zeta_e(l) - \zeta_e(r)]. \quad (4.4.3b)$$

As already mentioned, it is this difference in electrochemical potentials arising from the difference in electron concentrations on the two electrodes that provides the basic “driving force” for current through the external circuit, accompanied by internal workings of the electrochemical cell.

A trivial rearrangement of the above relation leads to a particular example of the so-called *Nernst equation*.

$$\mathcal{E} = (RT/2\mathcal{F}) \ln K_a - (RT/2\mathcal{F}) \ln \{a_{\pm}^2(l)/a_{\pm}^2(r)\} \quad (4.4.4a)$$

or

$$\mathcal{E} \equiv \mathcal{E}^0 - (RT/2\mathcal{F}) \ln \{a_{\pm}(l)/a_{\pm}(r)\}. \quad (4.4.4b)$$

in which we have introduced a *standard emf* by defining

$$\mathcal{E}^0 \equiv (RT/2\mathcal{F}) \ln K_a = -(\Delta G_d^0/2\mathcal{F}). \quad (4.4.4c)$$

Several remarks are in order: (i) \mathcal{E} is in a sense an “open-circuit voltage” that is developed by the cell, as shown in Eq. (4.4.3a). It is multiplied by $2\mathcal{F}$ to match the Gibbs free energy for the electrons participating in the specific reaction (4.4.1) at constant T and P . (ii) Since $\zeta_e(l) > \zeta_e(r)$ we note from Eq. (4.4.4c) that $\mathcal{E} > 0$ corresponds to a spontaneous operation of the cell for the reaction as written. In the contrary case the reaction proceeds in the opposite direction. (iii) Also, because of the manner in which we introduced the electrochemical potential for electrons, \mathcal{F} signifies the *magnitude* of the charge on a mole of electrons. (iv) The emf cited in Eq. (4.4.4) is specified solely by the *net chemical* reaction abstracted from Eq. (4.4.1), without reference to the presence of electrons. Therefore, ΔG_d just involves the electrochemical potentials of the *chemical species* participating in the operation of the galvanic cell. Then

$$\mathcal{E} = -(\Delta G_d^0/2\mathcal{F}), \quad (4.4.5)$$

again showing that a positive emf corresponds to the spontaneous cell operation. Emf measurements thus provide a direct evaluation of the differential free energy change of the net chemical reaction in the Daniell cell. This statement may be immediately generalized to encompass all galvanic processes operating in a similar manner. (v) The participation of electrons in the process has not “cancelled out” from Eq. (4.4.1); rather, the effect is subsumed in the definition for \mathcal{E} . The above discussion will now be generalized, as we show next.

Remarks

- 4.4.1.** One must be careful about signs here; the general expression $\sum_i \nu_i A_i = 0$ requires that we set $\nu_i > 0$ (< 0) for products (reagents). Therefore, the ionic species, and the electrons in the right compartment, as well as Zn in the left compartment (which are being used up and hence are labeled “reagents”), have been placed on the left hand side of the chemical equation, Eq. (4.4.1). The ionic and electronic contents of the left compartment, as well as Cu on the right compartment, involving positive ν_i (being generated, hence, labeled “products”) are placed on the right side of the chemical equation.
- 4.4.2.** The quantity ζ for a single electron has been multiplied by \mathcal{F} in order to put everything on a per mole basis. CuSO_4 (soln) and ZnSO_4 (soln) refer to undissociated species, dissolved in the saturated solution, that are in equilibrium with their respective ions and with the solid species.
- 4.4.3.** The term *electromotive force* is unfortunate, misleading, and out of touch with reality. However, it is so firmly entrenched that we will continue to use it here. Note that in Eq. (4.4.2) the definition involves the electrochemical potential of the electrons on the product side of the equation as written, minus that for the electrons on the reagent side for the reaction as written.

4.5 Galvanic Cells; Operational Analysis

The general operation of galvanic cells is symbolized by the overall “virtual reaction” $\sum_i \nu_i A_i = 0$, carried out only to an infinitesimal extent, which does not significantly alter the concentrations of chemical species or the emf. Advancement of the chemical reaction by $\delta\lambda$ units involves the transfer of $n\mathcal{F}\delta\lambda$ moles of electrons through the external circuit, where n is the number of equivalents, and \mathcal{F} is the Faraday (96,495 C). Work done by the surroundings in opposing the electron transfer is $n\mathcal{F}\delta\lambda \mathcal{E}$, the negative of the work performed by the cell. As shown in Eq. (1.9.10a), at constant T and P , reversibly executed work other than mechanical tracks the Gibbs free energy change: $\delta W_n = -\delta G$; therefore, the spontaneous virtual advancement of the process by $\delta\lambda$ units is specified by $n\mathcal{F}\mathcal{E}\delta\lambda = -(\delta G/\delta\lambda)_{T,P}\delta\lambda$, whence, as in Eq. (4.4.5), and for the reaction $\sum_i \nu_i A_i = 0$, as written,

$$n\mathcal{F}\mathcal{E} = -\Delta G_d = \sum_j \nu_j \mu_j|_{T,P}. \quad (4.5.1)$$

This important relation establishes the link between emf measurements and chemical thermodynamics. The above chemical potential will now be specified in terms of the hybrid system adopted in Eq. (3.4.4). (i) The standard state for pure solids or liquids participating in the electrochemical processes is that of the isolated material at temperature T under a pressure of 1 bar. (ii) For materials in homogeneous solid or liquid solution the standard state is chosen for each constituent at unit activity at 1 bar at the prevailing temperature. (iii) For gases participating in the chemical reaction the standard state is that of the ideal gas. Then, according to Eq. (3.4.4) and Eq. (4.5.1) we write

$$\mathcal{E} = \frac{RT}{n\mathcal{F}} \ln K_x - \frac{RT}{n\mathcal{F}} \left[\sum_s \nu_s \ln a_s^*(T, P) + \sum_j \nu_j \ln a_j(T, P, x_j) \right]. \quad (4.5.2)$$

Here s and j denote chemical species in the pure phase and in solution, respectively. In experiments at 1 bar the summation over s drops out. Conventionally, one introduces a *standard emf* by the expression

$$\mathcal{E}^0 = (RT/n\mathcal{F}) \ln K_x = -(\Delta G_d^0/n\mathcal{F}), \quad (4.5.3)$$

so that the operation of the cell is characterized through the open-circuit voltage

$$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{n\mathcal{F}} \left[\sum_s \nu_s \ln a_s^*(T, P) + \sum_j \nu_j \ln a_j(T, P, x_j) \right]. \quad (4.5.4)$$

Equation (4.5.4) is the (slightly generalized version of the) *Nernst equation*. Note that if a cell can be set up whose operation simulates the ionic, liquid, or gaseous reactions of interest, then a measurement of \mathcal{E}^0 directly evaluates the equilibrium parameter K_x .

Unified Description of Cell Operations

To characterize the general operating condition of a galvanic cell we need to establish a systematic nomenclature and a set of conventions that permit a unified description of galvanic cell operations. Consider as a representative example a cell at temperature T that consists of (i) a Pt electrode that is surrounded by gaseous hydrogen at pressure P and that is dipped into an HCl solution of molality m_l . The latter is connected via a salt bridge to a second compartment containing a saturated HCl solution in equilibrium with AgCl(s), at molality m_r , into which a silver electrode is immersed. The cell is at uniform temperature T . This cell is represented by the scheme



where the vertical bars separate distinct phases, and the double bar indicates that the two solutions are separated by a salt bridge that generates an internal emf of its own whose potential difference is considered below. Ordinarily, the emf of the salt bridge is small compared to all other contributions. The Pt electrode is inert but provides a needed interface for electron transfer to the external circuit.

We now introduce several conventions:

Convention 1: For the cell *as written* the oxidation process occurs on the left and reduction, on the right. Electrons move through the external circuit from left to right; conventional current

proceeds in the opposite direction. The redox reactions are schematized through the following half reactions: At the anode (left): $\frac{1}{2}\text{H}_2(P) = \text{H}^+(m_l) + \text{e}^-(l)$. The extra H^+ ions produced in this process are compensated for by the release of negative ions from the salt bridge or else the cations are absorbed into it; formally, this is representable as a transfer of Cl^- ions from right to left across the salt bridge. At the cathode (right) the following net process takes place: $\text{e}^-(r) + \text{AgCl}(s) = \text{Ag}(s) + \text{Cl}^-(m_r)$. The excess Cl^- ions produced thereby are compensated for by the release of positive ions from the salt bridge or the anions are absorbed into it; formally, this corresponds to the transfer of H^+ ions across the salt bridge. As explained in the previous section, the electron constituents in the half reactions should be ignored; they serve here only to balance out charges. The overall chemical reaction is thus given by $\frac{1}{2}\text{H}_2(P) + \text{AgCl}(s) = \text{Ag}(s) + \text{H}^+(m_l^+) + \text{Cl}^-(m_r^-)$, but in the final balanced equation the compensating cationic and anionic species in each compartment must be included in the chemical equation.

Convention 2: The cell emf for the cell as written is specified by the algebraic sum of two half-cell emfs:

$$\mathcal{E} = \mathcal{E}(l) - \mathcal{E}(r) = (\zeta_l - \zeta_r)/\mathcal{F}, \quad (4.5.5b)$$

where l and r refer to the left and right hand compartment for the cell as written; this reflects the splitting of the cell operation into the oxidative (l) and reductive (r) steps. In this example, $n = 1$.

Convention 3: The determination of \mathcal{E} is carried out systematically by first dealing with the standard emfs according to

$$\mathcal{E}^0 = \mathcal{E}_l^0 - \mathcal{E}_r^0, \quad (4.5.6)$$

where the overall standard emf has been written as an algebraic sum of the standard half-cell emfs for the left and right electrodes of the cell operation. Extensive tabulations of the \mathcal{E}^0 values are available. Conventionally, half reactions are written out as oxidation processes; hence, when using Eq. (4.5.6), the half reaction for the process (r) must be inverted, thereby changing the sign of the listed emf value.

Convention 4: The emf of a cell is positive when electrons flow spontaneously from the left to the right electrode through the external circuit.

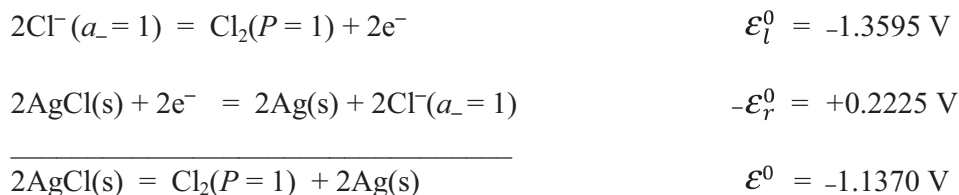
Convention 5: The standard electrode emf for the half reaction $\frac{1}{2}\text{H}_2(P = 1 \text{ bar}) = \text{H}^+(a_{\pm} = 1) + \text{e}^-$ is set to $\mathcal{E}_l^0 = 0$.

This last convention invokes the fact that emfs are generalized energies. They are thus known only to within an arbitrary constant that applies as well to all other emfs in the listing of half-cell standard emfs, thereby rendering everything self-consistent. The entries in the tabulations are determined experimentally by coupling the half cell of interest against the standard hydrogen electrode in the reducing mode. The measured total emf, \mathcal{E}^0 , is then the half emf of interest. Emfs so generated may serve as secondary standards for other half cells whose standard emfs are desired.

The above procedures are best illustrated by a specific example. Consider the cell



whose operation is governed by the half reactions, whose emf values are tabulated in the literature:



Note the sign reversal in listing \mathcal{E}_r^0 relative to the half reaction tabulation listing of $\mathcal{E}_r^0 = -0.2225 \text{ V}$ found in the literature. The contributions from the Cl^- ions cancel out, being at the same activity on both sides of the two half reactions. The electronic contributions are ignored for reasons specified earlier, but are written in to balance charges and to set $n = 2$ for the reaction as written. The emf in volts is given by

$$\mathcal{E} = -1.1370 - (RT/2\mathcal{F})\ln(a_{\text{Ag}}^2/a_{\text{AgCl}}^2) - (RT/2\mathcal{F})\ln a_{\text{Cl}_2}. \quad (4.5.8)$$

where the ratio $a_{\text{Ag}}^2/a_{\text{AgCl}}^2$ ordinarily does not differ significantly from unity, and where the activity for Cl_2 gas may usually be replaced by the prevailing Cl_2 pressure, P , over the anode.

Several remarks are in order. (i) Convince yourself that precisely the same emf expression would have been obtained if the cell operation had been written out as $\text{AgCl(s)} = \frac{1}{2}\text{Cl}_2(\text{g}) + \text{Ag(s)}$, with $n = 1$. Thus, the emf is independent of the manner in which the net reaction is balanced—a physically sensible result. (ii) The standard differential Gibbs free energy change for the net reaction $2\text{AgCl(s)} = \text{Cl}_2(P = 1) + 2\text{Ag(s)}$, $n = 2$, is therefore specified as follows: $\Delta G_d^0 = -2\mathcal{F}\mathcal{E}^0 = -2(96,485)(-1.1370) \text{ J} = 219,420 \text{ J}$, a very sizeable quantity. Since ΔG_d^0 is positive we infer that the reaction under SC occurs spontaneously in the opposite direction. Had the reaction been written as $\text{AgCl(s)} = \frac{1}{2}\text{Cl}_2(\text{g}) + \text{Ag(s)}$ we would have obtained $\Delta G_d^0 = 109,710 \text{ J}$. (iii) For the cell operation in reverse, as $\text{Ag(s), AgCl(s)} | \text{HCl}(a_{\pm} = 1) | \text{Cl}_2(a = 1), \text{Pt}$ one obtains $\mathcal{E}^0 = +1.1370 \text{ V}$, as well as $\Delta G_d^0 = -219,420 \text{ J}$. The foregoing reaction just written (with $\mathcal{E}^0 > 0$ and $\Delta G_d^0 < 0$) proceeds spontaneously. (iv) Silver tends to react spontaneously with Cl_2 gas to form AgCl , but under standard conditions this can be reversed by imposing an external counteracting emf slightly in excess of 1.1370 V .

4.6 Liquid Junction Potentials

A source of difficulty in electrochemical experiments is the generation of an emf when two dissimilar solutions in the cathode and anode regions are juxtaposed or connected by a salt bridge. Different ions in various solutions diffuse at different rates; the faster cations moving ahead of the slower ones set up an internal electric field that tends to retard their movement and to accelerate the slower cations. An analogous situation prevails for the anions. After a steady state sets in both types tend to move across the junction in the presence of an internal field; this is the origin of the junction emf.

Charges are carried by different ions in proportion to their transference numbers. Consider an infinite copy of the cell in which the two electrolyte compartments are separated by a salt

bridge of finite (small) width, stretching from point A to point B. Let a fraction t_i^+ of the positive charge be carried by cations with valence z_i^+ and a fraction t_j^- of the negative charge be transported by anions of valence $z_j^- = -|z_j^-|$. At each point in the junction under steady state, spontaneous conditions, t_i^+/z_i^+ equivalents of species i move across from right to left and $-t_j^-/|z_j^-|$ equivalents of species j are transported from left to right. The resulting increase in Gibbs free energy is given by

$$dG = \sum_i (t_i^+/z_i^+) d\mu_i^+ - \sum_j (t_j^-/|z_j^-|) d\mu_j^- \quad (4.6.1)$$

for each small layer perpendicular to the junction. The total change in Gibbs free energy across the entire junction J then reads

$$\Delta G_J = -\mathcal{F} \varepsilon_J = RT \sum_i \int \frac{t_i^+}{z_i^+} d \ln a_i^+ - RT \sum_j \int \frac{t_j^-}{|z_j^-|} d \ln a_j^- \quad (4.6.2)$$

in an obvious notation for the activities a . The integral runs over the entire domain A–B of the junction. The transference numbers may generally be replaced by average values \bar{t} , so that

$$\varepsilon_J = -\frac{RT}{\mathcal{F}} \sum_i \frac{\bar{t}_i^+}{z_i^+} \ln \frac{a_i^+(B)}{a_i^+(A)} + \frac{RT}{\mathcal{F}} \sum_j \frac{\bar{t}_j^-}{|z_j^-|} \ln \frac{a_j^-(B)}{a_j^-(A)}. \quad (4.6.3)$$

The individual ionic activities must be estimated by use of the Debye–Hückel theory. However, Eq. (4.6.3) shows that the cationic and anionic contributions tend to cancel out. Hence, except for a truly unusual situation in which a particular ratio $a(B)/a(A)$ exceeds a factor of 10, and/or where $t/|z|$ for a particular species is very large compared to all others, the emf remains well below the value of $RT/\mathcal{F} = 0.0592$ V at room temperature. Thus, junction potentials tend to be small compared to most emfs developed by cells. The effect may be further reduced by use of salt bridges that contain cations and anions of comparable mobility, so as to compensate for the tendency to develop internal emfs. The effect is also attenuated by employing parchment, agar–agar gels, or collodion to impede unbalancing ionic motion across the junction. In any event, junction potentials of the type described here tend to be small.

4.7 EMF Dependence on Activities

General Description

We first set up the general expression for the dependence of the galvanic cell emfs on the activity of the components participating in the cell reaction. Starting with the Nernst equation we find

$$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{n\mathcal{F}} \ln \left[\prod_s a_s^{\nu_s} (T, P) \prod_j a_j^{\nu_j} (T, P, m_j) \right], \quad (4.7.1)$$

where for the logarithmic argument Q at 300 K, $(RT/n\mathcal{F}) \ln Q = 0.05915 \log Q$, which includes the conversion from natural to common logarithms. The stoichiometry coefficients ν_s and ν_j are negative for the reagents in the cell reaction as written, and the activities a_j are generally referred to the

molalities m_j of the various components in the solid or liquid solution. The activities a_j may be determined by use of the Debye–Hückel limiting law at room temperature

$$\log \Gamma_{\pm}^{(m)} = -0.5092 z_+ |z_-| \sqrt{S_i} \quad (300 \text{ K}) \quad S_i \equiv (1/2) \sum_j z_j^2 m. \quad (4.7.2)$$

Thus, from a tabulation of standard emfs, from the specification of the a_s for pure phases as in Section 3.4, and from use of the Debye–Hückel limiting law, one can calculate the emf of the particular cell of interest. Usually, the procedure is used in reverse, whereby a measurement of \mathcal{E} yields the activity or activity coefficient for the solutes of interest.

Examples of Operating Cells

We now furnish several illustrations:

Consider the cell $\text{Pt}, \text{H}_2(P) | \text{HCl}(m) | \text{AgCl}(s), \text{Ag}(s)$ for which the half reactions are given by $\frac{1}{2}\text{H}_2(P) = \text{H}^+(m) + e^-$ and $e^- + \text{AgCl}(s) = \text{Cl}^-(m) + \text{Ag}(s)$, corresponding to the cell reaction $\frac{1}{2}\text{H}_2(P) + \text{AgCl}(s) = \text{Ag}(s) + \text{H}^+(m) + \text{Cl}^-(m)$. In this case

$$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{\mathcal{F}} \ln \frac{a_{\text{H}} + a_{\text{Cl}} - a_{\text{Ag}}}{a_{\text{H}_2}^{1/2} a_{\text{AgCl}}}, \quad (4.7.3)$$

which simplifies considerably for measurements carried out at 1 bar, where $a_{\text{Ag}}/a_{\text{H}_2}^{1/2} a_{\text{AgCl}} = 1$; also, we set $a_{\text{H}^+} a_{\text{Cl}^-} = a_{\pm}^2$, so that

$$\mathcal{E} = \mathcal{E}^0 - \frac{2RT}{\mathcal{F}} \ln a_{\pm}(m), \quad (P = 1 \text{ bar}). \quad (4.7.4)$$

To determine the activity coefficient, without prior knowledge of \mathcal{E}^0 , rewrite the above as

$$\mathcal{E} + \frac{2RT}{\mathcal{F}} \ln m_{\pm} = \mathcal{E}^0 - \frac{2RT}{\mathcal{F}} \ln \Gamma_{\pm}^{(m)}. \quad (4.7.5)$$

Now introduce the extended Debye–Hückel equation, Eq. (4.2.5); on setting $z_+ = z_- = \nu_+ = \nu_- = 1$ and $S_i = \sqrt{m_{\pm}}$ for the case at hand we obtain (300 K)

$$\mathcal{L} = \mathcal{E} + 0.11833 \left[\log m_{\pm} - \frac{0.5092 \sqrt{m_{\pm}}}{1 + \sqrt{m_{\pm}}} \right] \equiv \mathcal{E}^0 - 0.11833 S m_{\pm}. \quad (4.7.6)$$

Measurements of \mathcal{E} are then taken for several HCl solutions at different molalities; then a plot of \mathcal{L} vs m_{\pm} should yield a straight line in the range where the extended Debye–Hückel equation holds. Extrapolation of this line to $m_{\pm} = 0$ yields \mathcal{E}^0 , and the slope is proportional to S . One then returns to Eq. (4.7.5) to find the $\Gamma_{\pm}(m)$ values for each set of measured \mathcal{E} and m_{\pm} values. Very accurate measurements of the activity coefficient thus become available.

As a second example consider the operation of an electrolytic fuel cell according to the scheme: $\text{Pt}, \text{H}_2(P_{\text{H}}) | \text{NaOH}(m) | \text{O}_2(P_{\text{O}}), \text{Pt}$, with half reactions $4\text{OH}^-(m) + 2\text{H}_2(P_{\text{H}}) = 4\text{H}_2\text{O}(\ell) + 4e^-$ and

$\text{O}_2(P_{\text{O}}) + 2\text{H}_2\text{O}(\ell) + 4\text{e}^- = 4\text{OH}^-(m)$, yielding a net reaction $2\text{H}_2(P_{\text{H}}) + \text{O}_2(P_{\text{O}}) = 2\text{H}_2\text{O}(\ell)$. Correspondingly,

$$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{4\mathcal{F}} \ln \left[\frac{a_{\text{H}_2\text{O}}^2}{a_{\text{H}_2}^2(P_{\text{H}_2})a_{\text{O}_2}(P_{\text{O}_2})} \right] \approx \mathcal{E}^0 + \frac{RT}{2\mathcal{F}} \ln P_{\text{H}_2}P_{\text{O}_2} - \frac{RT}{2\mathcal{F}} \ln a_{\text{H}_2\text{O}}. \quad (4.7.7)$$

Ordinarily, the contribution from the last term is negligible. We also find $\Delta G_d = -4\mathcal{F}\mathcal{E}$ which, at a cell voltage of $\mathcal{E} = 1.23$ V, corresponds roughly to 475 kJ/mol. In principle, the fuel cell represents a good source for energy delivery, but there are problems in rendering such a cell truly practical.

As a final example consider the lead storage cell that involves the following configuration: $\text{Pb}|\text{PbSO}_4(\text{s})|\text{H}_2\text{SO}_4(\text{aq})|\text{PbSO}_4(\text{s})|\text{PbO}_2(\text{s})|\text{Pb}$. The corresponding half reactions are given by



for a net reaction



Omitting the contributions of the solid constituents, the emf generated by this cell reads

$$\mathcal{E} = \mathcal{E}^0 - (RT/2\mathcal{F}) \ln \left(a_{\text{H}_2\text{O}}^2 / a_{\pm\text{H}_2\text{SO}_4(\text{aq})}^4 \right), \quad (4.7.9)$$

which under normal conditions generates an emf of roughly 2 V. The cell is commonly used in many practical applications because it is readily reversible, can undergo many charge and discharge cycles, and provides large current densities under nonequilibrium conditions.

Types of Operating Cells

We review several types of galvanic cells in common use.

- (a) *Chemical cells.* Several examples of this type have been cited in the previous sections. As an additional case we consider the cell $\text{Zn}(\text{s})|\text{ZnCl}_2(m)|\text{AgCl}(\text{s}), \text{Ag}(\text{s})$, with a net chemical reaction $\text{Zn}(\text{s}) + 2\text{AgCl}(\text{s}) = 2\text{Ag}(\text{s}) + \text{Zn}^{2+}(m) + 2\text{Cl}^-(2m)$. By the procedures described earlier we find

$$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{2\mathcal{F}} \ln \left(\frac{a_{\text{Ag}(\text{s})}^2}{a_{\text{AgCl}(\text{s})}^2 a_{\text{Zn}(\text{s})}} \right) - \frac{RT}{2\mathcal{F}} \ln (a_{\text{Zn}^{2+}} a_{\text{Cl}^-}^2) = \mathcal{E}^0 - \frac{RT}{2\mathcal{F}} \ln \left(\frac{a_{\text{Ag}(\text{s})}^2}{a_{\text{AgCl}(\text{s})}^2 a_{\text{Zn}(\text{s})}} \right) - \frac{3RT}{2\mathcal{F}} \ln a_{\pm}. \quad (4.7.10)$$

If one specifies the activities of the solids as described in Section 3.4 (ordinarily very close to unity) then a measurement of the cell emf yields the mean molal activity coefficient of ZnCl_2 in solution.

- (b) *Electrode concentration cell:* Here a mirror image cell is set up in which the electrodes differ solely in the concentration of surroundings. As an illustration consider the cell $\text{Zn}, \text{Hg}(m_l)|\text{ZnSO}_4(m)|\text{Hg}(m_r), \text{Zn}$ in which a zinc amalgam paste serves as the reactive

electrode. The half reactions are given by $\text{Zn}(m_l) = x\text{Zn}^{2+}(m_l) + 2xe^-$ and $x\text{Zn}^{2+}(m_r) + 2xe^- = \text{Zn}(m_r)$, with the net reaction $\text{Zn}(m_l) = \text{Zn}(m_r)$; i.e., Zn has been reversibly transferred from the amalgam on the left to the amalgam on the right. Obviously, the standard state corresponds to $a_l = a_r$, so that $\mathcal{E}^0 = 0$. Then,

$$\mathcal{E} = (RT/n\mathcal{F})\ln(a_l/a_r) \quad n = 2x, \quad (4.7.11)$$

where x is the molecular aggregation of Zn in the amalgam.

As a second example, consider the reversible transfer of gas from the left to the right compartment of the particular cell $\text{Pt}, \text{H}_2(P_l) | \text{HCl}(m) | \text{H}_2(P_r), \text{Pt}$. The half reactions are given by $\text{H}_2(P_l) = 2\text{H}^+(m_+) + 2e^-$ and $2\text{H}^+(m_+) + 2e^- = \text{H}_2(P_r)$, with the net transfer $\text{H}_2(P_l) = \text{H}_2(P_r)$. The corresponding emf is given by

$$\mathcal{E} = (RT/2\mathcal{F})\ln(a_l/a_r). \quad (4.7.12)$$

Clearly, $\mathcal{E} > 0$, $\Delta G_d < 0$ or $\mathcal{E} < 0$, $\Delta G_d > 0$ according as $P_l > P_r$ or $P_l < P_r$, respectively; in accord with intuition, the transfer always occurs in the direction from the higher to the lower pressure compartment.

(c) Concentration cells with liquid junctions: As an example in this category consider the cell $\text{Ag}(s) | \text{AgNO}_3(m_l) || \text{AgNO}_3(m_r) | \text{Ag}(s)$. In an infinite copy of this cell one equivalent of silver enters into solution on the left, and one equivalent is deposited on the electrode on the right, accompanied by the electron transfer of 1 F through the external circuit. We analyze the overall process in several steps: n_l and n_r are the mole numbers of the species in the left and right compartments, and t_+ and t_- represent transference numbers for Ag^+ and NO_3^- ions, respectively.

- (i) Initially there are n_l and n_r moles of Ag^+ as well as of NO_3^- present in the left and right compartments, respectively.
- (ii) The passage of 1 \mathcal{F} of charge through the external circuit incurs a change in cation concentration, such that at the conclusion $n_l + 1$ and $n_r - 1$ moles of Ag^+ are present in the respective compartments.
- (iii) Simultaneously, there occurs a cation transfer of t_+ moles of Ag^+ across the liquid junction from left to right; $n_l + 1 - t_+$ moles of cations remain on the left and $n_r - 1 + t_+$ moles are found on the right. Actually, in a KCl salt bridge normally used it is the K^+ compensating ions that move across the bridge.
- (iv) There also occurs an anion transfer of t_- mole of NO_3^- across the liquid junction in the opposite direction: now $n_l + t_-$ moles of the anion are present on the left and $n_r - t_-$ moles remain on the right. Actually, when a KCl salt bridge is used it is Cl^- ions that move across the bridge.
- (v) With $t_+ = 1 - t_-$, the final formal tally is as follows: $n_l + t_-$ moles of Ag^+ and NO_3^- are present in the left compartment and $n_r - t_-$ moles of Ag^+ and NO_3^- are present on the right.

The above five formal steps (ignoring changes introduced by the functioning of the salt bridge) lead to the net reaction $t_- \text{Ag}^+(a_+)_r + t_- \text{NO}_3^-(a_-)_r = t_- \text{Ag}^+(a_+)_l + t_- \text{NO}_3^-(a_-)_l$. One sees that the left-to-right external electron flow is compensated for in part by transfer of Ag^+ ions past the junction in the same direction, and in part, by transfer of NO_3^- ions in

the opposite direction, in proportion to their transference numbers. All steps occur in proper synchronization so that electroneutrality is strictly preserved. The emf for this cell is thus given by

$$\mathcal{E} = -\frac{RT}{\mathcal{F}} \ln \left[\frac{a_+(l)a_-(l)}{a_+(r)a_-(r)} \right]^{t_-} = 2 \frac{t_- RT}{\mathcal{F}} \ln \frac{a_{\pm}(r)}{a_{\pm}(l)}. \quad (4.7.13)$$

Note how the transference number for the anion appears in this expression. In fact, the analysis is usually carried through in reverse: from a measurement of \mathcal{E} one may determine the transference number.

(d) Double concentration cells: An example is furnished by the cell

$\text{Zn(s)}|\text{ZnSO}_4(m_l), \text{Hg}_2\text{SO}_4(\text{s})|\text{Hg}(\ell)|\text{Hg}_2\text{SO}_4(\text{s}), \text{ZnSO}_4(m_r)|\text{Zn(s)}$, for which the sparingly soluble salt Hg_2SO_4 furnishes some Hg^{2+} ions to the solution for transfer into or out of the $\text{Hg}(\ell)$ compartment; the SO_4^{2-} concentration in both solutions remains essentially constant. Under normal conditions $m_l, m_r \gg m(\text{Hg}^{2+})$; thus, one assumes that $m(\text{Zn}^{2+}) = m(\text{SO}_4^{2-})$. The left hand operation is analyzed by the sequence: $\text{Zn(s)} = \text{Zn}^{2+}(m_l) + 2\text{e}^-$, followed by $2\text{Hg}^+(m') + 2\text{e}^- = 2\text{Hg}(\ell)$, then, by $\text{Hg}_2\text{SO}_4(\text{s}) = 2\text{Hg}^+(m') + \text{SO}_4^{2-}(m_l)$, which yields a net reaction $\text{Zn(s)} + \text{Hg}_2\text{SO}_4(\text{s}) = \text{Zn}^{2+}(m_l) + \text{SO}_4^{2-}(m_l) + 2\text{Hg}(\ell)$. Similarly, on the right the reaction proceeds according to the scheme $\text{Zn}^{2+}(m_r) + \text{SO}_4^{2-}(m_r) + 2\text{Hg}(\ell) = \text{Zn(s)} + \text{Hg}_2\text{SO}_4(\text{s})$. The overall reaction now reads $\text{Zn}^{2+}(m_r) + \text{SO}_4^{2-}(m_r) = \text{Zn}^{2+}(m_l) + \text{SO}_4^{2-}(m_l)$, for which the emf is specified by

$$\mathcal{E} = -\frac{RT}{2\mathcal{F}} \ln \left[\frac{a_+(l)a_-(l)}{a_+(r)a_-(r)} \right] = \frac{RT}{\mathcal{F}} \ln \frac{a_{\pm}(r)}{a_{\pm}(l)}. \quad (4.7.14)$$

This is clearly another example of a concentration cell.

Queries

- 4.7.1** Do the two galvanic cells $\text{Cu(s)}|\text{Cu}^{2+} \parallel \text{Cu}^+|\text{Cu(s)}$ and $\text{Pb(s)}|\text{Cu}^{2+} \parallel \text{Cu}^+|\text{Cu(s)}$ have the same standard emf values? Explain.
- 4.7.2** Is there a difference in operation and in emf for the two cells $\text{Pt, H}_2(P)|\text{HCl}(x_1) \parallel \text{HCl}(x_2)|\text{AgCl(s), Ag(s)}$ and $\text{Pt}|\text{H}_2(P)|\text{HCl}(x_1)|\text{AgCl(s), Ag(s)}$? Justify your answer.

4.8 Thermodynamic Information from Galvanic Cells

Measurements of the emf of galvanic cells are used to advantage to extract thermodynamic information on chemical reactions. As earlier stated, corresponding to the symbolic chemical reaction $\sum_j \nu_j \text{A}_j = 0$, one may specify an equilibrium parameter $K_x = \prod_s a_s^{\nu_s} / \prod_j a_j^{\nu_j}$. If a cell can be devised in which the cell operation reproduces the reaction $\sum_j \nu_j \text{A}_j = 0$ then the relations

$$\mathcal{E} = -\Delta G_d/n\mathcal{F} \quad (4.8.1a)$$

$$\mathcal{E}^0 = -(\Delta G_d^0/n\mathcal{F}) = (RT/n\mathcal{F})\ln K_x \quad (4.8.1b)$$

may be applied. Thus, both the (standard) differential Gibbs free energies and the equilibrium constants can be determined once \mathcal{E} and \mathcal{E}^0 are known. From the relation $\Delta S_d = -(\partial G_d/\partial T)_{P,n_i}$ one immediately obtains information concerning the differential entropies of the reaction, namely,

$$\Delta S_d = n\mathcal{F}(\partial \mathcal{E}/\partial T)_{P,n_i}; \quad \Delta S_d^0 = n\mathcal{F}(\partial \mathcal{E}^0/\partial T)_{P,n_i}. \quad (4.8.2)$$

Finally, the Gibbs–Helmholtz relation may be applied to find the corresponding enthalpies, namely,

$$\Delta H_d = -n\mathcal{F} \left[\mathcal{E} - T(\partial \mathcal{E}/\partial T)_{P,n_i} \right]; \quad \Delta H_d^0 = -n\mathcal{F} \left[\mathcal{E}^0 - T(\partial \mathcal{E}^0/\partial T)_{P,n_i} \right]. \quad (4.8.3)$$

The above shows how important thermodynamic information may be obtained from convenient emf measurements of cells that undergo chemical reactions of interest.

Assignment

4.8.1. Derive equations relating $\Delta C_P|_d$ and ΔV_d for chemical reactions to emf measurements.

Thermodynamic Properties of Materials in Externally Applied Fields

5

5.0 Introductory Comments

In this chapter, you will be introduced to the thermodynamic properties of materials subjected to several types of external fields: gravitational, centrifugal, surface, radiation, electric, and magnetic fields. The analysis gives rise to several new effects that are of intrinsic interest; they also provide new insights on the systematics of thermodynamic analysis. Please note these features in our subsequent discussion.

5.1 Thermodynamics of Gravitational and Centrifugal Fields

Generalities

To handle gravitational effects, consider a tall, vertical cylinder of height h and cross-section A (Figure 5.1.1), containing a fixed number of gas molecules of various chemical species at uniform temperature T in the earth's gravitational field.¹ To cope with the nonuniform distribution of the gas molecules, we divide the container into volume elements of cross-section A and vertical extension dz . Material contained in each of the infinitesimal layers is characterized by an energy density u , an entropy density s , and a concentration c_i for species i . The total energy U , entropy S , and mole number n_i of species i is then given by

$$U = \int_0^h u A dz; \quad S = \int_0^h s A dz; \quad n_i = \int_0^h c_i A dz. \quad (5.1.1)$$

Each element of height dz clearly constitutes an open system whose properties depend on z . The total energy U includes contributions from both the internal energy E and from the gravitational potential energy.

Consider a typical volume element of cross-section A and height dz , located at elevation z with respect to an arbitrarily chosen reference. Any change in its internal energy E is subject to the first law,

$$dE(z) = TdS(z) - P(z)dV(z) + \sum_i \mu_i(z)dn_i(z), \quad (5.1.2)$$

in which allowance has been made for the variation of all properties except temperature with height. The total energy of the subsystem, including gravitational effects, is given by

$$dU(z) = dE(z) + \sum_i M_{ig}z dn_i(z). \quad (5.1.3)$$

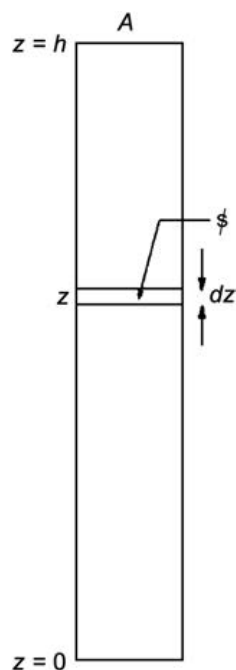


FIGURE 5.1.1

Cylinder of cross-section A in the earth's gravitational field. A subsystem of thickness dz is shown at height z above ground level $z = 0$.

Here, M_i represents the gram molecular mass of species i , and g , the gravitational constant. The expression shows explicitly how the total energy in the volume element changes through the influx or outflow of gaseous species through any particular volume element.

On combining Eq. (5.1.2) with Eq. (5.1.3), we obtain the total energy of material at height z as

$$dU(z) = TdS(z) - P(z)dV(z) + \sum_i [\mu_i(z) + M_i g z] dn_i(z). \quad (5.1.4)$$

The combination $\mu_i(z) + M_i g z$ occurs so often in the subsequent analysis that it is convenient to assign it a new symbol,

$$\zeta_i(z) \equiv \mu_i(z) + M_i g z, \quad (5.1.5)$$

which may be called the *gravochemical potential*; it is an obvious generalization of the ordinary chemical potential. Thence,

$$dU(z) = TdS(z) - P(z)dV(z) + \sum_i \zeta_i(z) dn_i(z). \quad (5.1.6)$$

In the present case, equilibrium conditions are best dealt with by introducing the modified Helmholtz free-energy function as²

$$F_g(z) = U(z) - TS(z). \quad (5.1.7)$$

from which one obtains the differential form

$$dF_g(z) = -S(z)dT - P(z)dV(z) + \sum_i \zeta_i(z)dn_i(z). \quad (5.1.8)$$

Equilibrium conditions are enforced by subjecting the subsystem to a virtual displacement for which $\delta F_g|_{T,V} = 0$, subject to the requirement that the number of moles of the various species i in the entire cylinder remain fixed: $\delta n_i = 0$. For this purpose, we introduce a Helmholtz free-energy density f_g by the relation $F_g = \int_0^h f_g(z)Adz$. We then use the properties introduced in Eq. (5.1.1) and consider a fixed element of volume, Adz , to rewrite Eq. (5.1.4) as

$$d[u(z)Adz] = Td[s(z)Adz] + \sum_i \zeta_i(z)d[c_i(z)Adz]. \quad (5.1.9)$$

The equilibrium constraint, as specified by Eqs. (5.1.7) and (5.1.9), thus reads

$$\begin{aligned} 0 = \delta F_g|_{T,V} &= \int_0^h \delta[f_g(z)Adz]|_{T,V} = \int_0^h \delta[u(z)Adz]|_{T,V} - T \int_0^h \delta[s(z)Adz]|_{T,V} \\ &= \int_0^h \sum_i \zeta_i(z) \delta[c_i(z)Adz]|_{T,V}. \end{aligned} \quad (5.1.10)$$

The auxiliary constraint is given by

$$\delta n_i|_{T,V} = 0 = \int_0^h \delta(c_i(z)Adz). \quad (5.1.11)$$

The minimization is carried out using the usual Lagrangian multiplier technique: we minimize the enlarged function $F_g - \sum_i \lambda_i n_i$, where the λ_i are the undetermined multipliers. Thus, we write

$$\int_0^h \sum_i \zeta_i(z) \delta[c_i(z)Adz]|_{T,V} - \sum_i \lambda_i \int_0^h \delta[c_i(z)Adz]|_{T,V} = 0. \quad (5.1.12)$$

This condition can be met uniquely if and only if the integrands match for every i , so that

$$\zeta_i = \mu_i(z) + M_i g z = \lambda_i (\text{a constant}). \quad (5.1.13)$$

The above requirement is remarkable: although μ_i and $M_i g z$ individually vary with z , their sum does not. We now examine the consequences.

The Barometric Formula

Consider a single chemical species obeying the perfect gas law. With T constant, we write the chemical potential as $d\mu = (V/n)dP$. We seek to determine the variation of P with z . For this purpose, we write

$$(d\mu/dz) = (V/n)(dP/dz) = (d\zeta/dz) - Mg = -Mg(\text{constant } T), \quad (5.1.14)$$

where the right-hand side follows because, by Eq. (5.1.13), ζ does not depend on z . For a perfect gas, the above relation becomes

$$(RT/P)(dP/dz) = RT(d \ln P/dz) - Mg, \quad (5.1.15a)$$

or, in integrated form,

$$P = P_0 \exp(-Mgz/RT), \quad (5.1.15b)$$

where P_0 is the pressure at height $Z = 0$. The above represents the well-known barometric formula for the dependence, at constant temperature, of the ideal gas pressure on distance z above ground level.

Systematics of Thermodynamics in the Presence of a Gravitational Field

A more systematic treatment of thermodynamic effects in a gravitational field is provided by rewriting Eq. (5.1.6) for the internal energy of a single species in a small volume element at location z as

$$dU = TdS - PdV + \psi dn + \mu dn, \quad (5.1.16a)$$

in which we have set $\psi \equiv Mgz$ as the molar gravitational potential of the species under consideration, and where $\zeta = \psi + \mu$. We now introduce the conventional Legendre transformations: $H = U + PV$, $F_g = U - TS$, and $G = H - TS$ to obtain

$$dH = TdS + VdP + \psi dn + \mu dn \quad (5.1.16b)$$

$$dF_g = -SdT - PdV + \psi dn + \mu dn \quad (5.1.16c)$$

$$dG = -SdT + VdP + \psi dn + \mu dn. \quad (5.1.16d)$$

In principle, one could generate four additional functions of state of the form $Y' = Y - \psi n$ whose differential forms dY' would involve $-nd\psi$ in place of $+\psi dn$ in the various resulting differential forms of the state functions. However, such a step does not lead to any useful results since gravitational fields normally considered in thermodynamic treatments are not subject to variation.

Note that we have introduced a new set of conjugate variables, namely (ψ, n) that play a role in determining gravitational field effects. One may readily find expressions for T , P , V , S , ψ , and μ by straightforward differentiation of the appropriate function of state listed in Eqs. (5.1.16), in analogy to the procedure of Section 1.12. Similarly, one may undertake a double differentiation in either order of the type $\partial^2 Y / \partial x_i \partial x_j = \partial^2 Y / \partial x_j \partial x_i$ to obtain the relevant Maxwell equations; only a small fraction of these produces useful relations. Here the condition of keeping ψ constant is equivalent to maintaining each subsystem of extension dz at constant elevation z .

The above procedure again illustrates the methodological approach to thermodynamics.

Effect of Centrifugal Forces

Let a cylindrical vessel rotate about a fixed axis with a steady angular velocity. In this case, a point mass m at a distance r from the rotation axis is acted on by a force $f = m\omega^2 r$ in the direction along decreasing r to keep it moving in a circular path about the origin. The corresponding potential energy, i.e. the potential involved in keeping the mass at point r is given by

$$\widehat{W} = - \int_0^r m\omega^2 r dr = -\frac{1}{2} m\omega^2 r^2, \quad (5.1.17a)$$

and the differential increase corresponding to the placement of additional mass $M_i dn_i$ of species i at that point is specified by

$$d\widehat{W} = -\frac{1}{2} M_i \omega^2 r^2 dn_i. \quad (5.1.17b)$$

This result may be compared with Eq. (5.1.3): it is seen that the relations derived for gravitational field effects may be carried over to the present case by replacing gz in the previous subsection with $-\frac{1}{2}\omega^2 r^2$. The subsequent portion of the derivation may be taken over without change; in particular, we obtain in place of Eq. (5.1.13) the relation

$$\zeta_i = \mu_i(r) - \frac{1}{2} M_i \omega^2 r^2 = \lambda_i (\text{a constant}). \quad (5.1.18)$$

At constant temperature and pressure, the generalized chemical potential is constant but the chemical potential itself changes with r to the extent that pressure and composition do. Let $d\mu_i|_{T,P}$ represent the change in chemical potential due to alterations in composition; Eq. (5.1.18) in differential form then specializes to (T constant)

$$d\mu_i|_{T,P} + \bar{V}_i dP - M_i \omega^2 r dr = 0, \quad (5.1.19a)$$

where the middle term derives from the partial differential of ζ_i with respect to P . Let x_i be the mole fraction of i at location r , then Eq. (5.1.19a) may be rewritten as (T constant)

$$\sum_i x_i d\mu_i|_{T,P} + \sum_i x_i \bar{V}_i dP - \sum_i x_i M_i \omega^2 r dr = 0. \quad (5.1.19b)$$

The first term in the above drops out because of the Gibbs–Duhem relation. The remainder may be recast in the form

$$dP = \frac{\sum_i x_i M_i}{\sum_i x_i \bar{V}_i} \omega^2 r dr = \rho \omega^2 r dr, \quad (5.1.19c)$$

where ρ is the density of the constituent material at point r . We next substitute Eq. (5.1.19c) into Eq. (5.1.19a) to obtain

$$d\mu_i|_{T,P} - \left(M_i - \bar{V}_i \frac{\sum_j x_j M_j}{\sum_j x_j \bar{V}_j} \right) \omega^2 r dr = 0. \quad (5.1.20)$$

Pressure of Gases in a Centrifugal Field

One may integrate Eq. (5.1.19c) after specifying how ρ varies with r . On the assumption that the centrifugal contribution is “small,” this dependence may be neglected. Then, at a distance r from the rotation axis

$$P = P_0 + \frac{1}{2} \rho \omega^2 r^2, \quad (5.1.21)$$

where P_0 is the pressure encountered at the rotation axis. For ideal gases, we adopt the relation $\rho = MP/RT$. Then we obtain from Eq. (5.1.19c)

$$RT d \ln P = M \omega^2 r dr, \quad (5.1.22)$$

which assumes the integrated form

$$\ln(P/P_0) = M\omega^2 r^2 / 2RT. \quad (5.1.23)$$

We see that the pressure of the gas relative to P_0 , its value at $r = 0$, rises exponentially as the square of the distance away from the rotation axis and as the square of the angular rotation speed. All this, of course, holds only after the entire mass of gas has assumed the same state of uniform rotation as the container. Recall again that the dependence of ρ on r has been neglected.

For a mixture of gases, we return to Eq. (5.1.19a) to write $d\mu_i|_{T,P} = RTd \ln x_i$, $P_i = x_i P$, and $\bar{V}_i = RT/P$ to obtain

$$d \ln P_i = (M_i \omega^2 r^2 / RT) dr, \quad (5.1.24a)$$

or, in integrated form,

$$\ln(P_i/P_{i0}) = M_i \omega^2 r^2 / 2RT. \quad (5.1.24b)$$

For a two-component ideal gaseous mixture, this may be recast as follows: since $x_1/x_2 = P_1/P_2$ and $x_{10}/x_{20} = P_{10}/P_{20}$, we obtain

$$\ln(x_1 x_{20} / x_2 x_{10}) = (M_1 - M_2) \omega^2 r^2 / 2RT, \quad (5.1.25)$$

which indicates that the separation effect becomes exponentially more pronounced with the difference in mass of the two components and with the square of the angular velocity and the square of its distance from the rotation axis.

Binary Ideal Liquid Solutions in Centrifugal Fields

Here we again set $d\mu_i|_{T,P} = RTd \ln x_i$; Eq. (5.1.20) then assumes the following forms:

$$RTd \ln x_1 = \left[M_1 - \bar{V}_1 \left(\frac{x_1 M_1 + x_2 M_2}{x_1 \bar{V}_1 + x_2 \bar{V}_2} \right) \right] \omega^2 r dr \quad (5.1.26a)$$

$$RTd \ln x_2 = \left[M_2 - \bar{V}_2 \left(\frac{x_1 M_1 + x_2 M_2}{x_1 \bar{V}_1 + x_2 \bar{V}_2} \right) \right] \omega^2 r dr. \quad (5.1.26b)$$

Multiplication with \bar{V}_i , followed by subtraction of these relations, leads to

$$RT(\bar{V}_2 d \ln x_1 - \bar{V}_1 d \ln x_2) = (M_1 \bar{V}_2 - M_2 \bar{V}_1) \omega^2 r dr, \quad (5.1.27)$$

which may be integrated to yield

$$RT \left(\bar{V}_2 \ln \frac{x_1}{x_{10}} - \bar{V}_1 \ln \frac{x_2}{x_{20}} \right) = (M_1 \bar{V}_2 - M_2 \bar{V}_1) \omega^2 r^2 / 2. \quad (5.1.28)$$

Since $(M_1 \bar{V}_2 - M_2 \bar{V}_1) = M_1 M_2 (\bar{V}_2 / M_2 - \bar{V}_1 / M_1)$, one observes that there will be no separation in composition of the liquid unless the specific volumes of the two components differ. In that case, the degree of separation rises exponentially as $\omega^2 r^2$.

Comment and Exercises

- 5.1.1. Provide reasons why a gas in a gravitational potential does not simply settle at the bottom of the tall, vertical cylinder, where its potential energy would be least. It may be helpful to note, on a microscopic scale, that the accumulation of gas at the bottom will set up a vertical diffusion gradient. Can you provide a second argument that invokes the entropy of the gas?
- 5.1.2. In this section, we temporarily designate the Helmholtz free energy by F_g to prevent confusion with the symbol A for cross-sectional area.
- 5.1.3. In contrast to the discussion of the text, assume that adiabatic conditions apply to an ideal gas maintained in a tall, vertical cylinder. Derive an expression relating dP and dT ; then find an expression for dP in terms of dz . Next, determine $dT/dz = (\partial T/\partial P)S(\partial P/\partial Z)$ and integrate to determine $T(z)$. Take $C_P/C_V = 1.41$, $M = 29$ g/mol for air, $g = 980$ cm/s² and determine the approximate change in temperature per kilometer of elevation.
- 5.1.4. Determine all possible Maxwell relations based on Eqs. (5.1.16).
- 5.1.5. Prove that for a binary mixture involving mole fractions x_1 and x_2 , the following relation holds: $RT \ln(x_1 x_2^0 / x_2 x_1^0) = (M_2 - M_1)gz$; the superscripts denote values of x at ground level.
- 5.1.6. Determine the energy and entropy of an ideal gas distributed at constant T in a tall, vertical cylinder of height h .
- 5.1.7. Compare the effect of placing 1 g of material in the earth's gravitational field as against placing 1 g at a distance of 6 cm away from the axis of a cylinder rotating at a speed of 40 revolutions/s. Comment on the ratio of the two forces.

5.2 Thermodynamics of Adsorption Processes

We next consider the adsorption of gases on surfaces. This problem not only is of intrinsic interest but also provides valuable pedagogical insights that obtain when new choices for thermodynamic functions of state are introduced. At the outset, we must investigate the new degrees of freedom needed to characterize an adsorption process. We consider a system consisting of a very thin layer of atoms held on the surface of a material exposed to a gas phase. The bulk solid or liquid is termed the *adsorbent*, while the material held on its surface is termed the *adsorbate*. The process by which material is transferred from the gas to the surface phase is called *adsorption*.

As an illustration, consider the deposit of a thin film of moisture on a windshield of a car left overnight in cold weather. Here the windshield and condensed moisture may be regarded as adsorbent and adsorbate, respectively. The condensation has occurred because at the prevailing temperature, the saturation vapor pressure has been exceeded. The analogy is somewhat inaccurate because in the processes considered later we restrict attention to adsorbates consisting of at most a few atomic layers.

The adsorbate forms a separate thermodynamic phase in its own right, characterized by a volume V_s , an entropy S_s , mole numbers n_s for each species, and its own chemical potential μ_s . At equilibrium, the temperature T and pressure P for the adsorbate matches that of the gas phase. To handle adsorption effects, a new thermodynamic variable is introduced, namely the surface area A_s , which governs the amount of material that can be adsorbed. This is the case because an adsorbent in single-crystal form has a much smaller surface area than the same amount that has been crushed to a fine powder. We thus

introduce A_s as a new control variable that plays a role for adsorbates similar to the volume, V_g , for bulk materials. Associated with this new degree of freedom, one must look for a conjugate intensive variable, the two-dimensional spreading pressure ϕ ; for, according to Section 1.5, the element of work involved in an infinitesimal increase dA_s in surface area is specified by $-\phi dA_s$. Moreover, the function $\phi = \phi(V_s, A_s, n_s, T)$ represents an equation of state for the surface phase analogous to the function $P = P(V_g, n_g, T)$ for the gas phase. For a more sophisticated introduction of the set of the above conjugate variables, you should consult specialized sources.¹

Thermodynamic Functions for the Adsorbate

On introducing ϕ and A_s as conjugate variables, we write the first law of thermodynamics in the form

$$dE_s = TdS_s - PdV_s - \phi dA_s + \mu_s dn_s. \quad (5.2.1)$$

From the above, we can now immediately derive several other functions of state, using the customary Legendre transformations. By strict analogy to Section 1.12, we may define an enthalpy

$$H'_s = E_s + PV_s, \quad (5.2.2a)$$

a Helmholtz free energy (*N.B. in this section we denote this quantity by F_s to avoid confusion with the symbol A_s for surface area*),

$$F_s = E_s + TS_s, \quad (5.2.2b)$$

and a Gibbs free energy

$$G'_s = H'_s - TS_s, \quad (5.2.2c)$$

However, it is perfectly appropriate to introduce another set of functions of state, namely, another energy,

$$E'_s = E_s + \phi A_s, \quad (5.2.2d)$$

another enthalpy,

$$H_s = H'_s + \phi A_s, \quad (5.2.2e)$$

another Helmholtz free energy,

$$F'_s = E'_s - TS_s, \quad (5.2.2f)$$

and another Gibbs free energy,

$$G_s = H_s - TS_s. \quad (5.2.2g)$$

No one set of state functions is to be preferred over any other; all physical predictions ultimately depend on the experimental operational conditions, as we shall show. The differential forms are easily seen to be the following:

$$dE_s = TdS_s - PdV_s - \phi dA_s + \mu_s dn_s \quad (5.2.3a)$$

$$dH_s = TdS_s + V_s dP + A_s d\phi + \mu_s dn_s \quad (5.2.3b)$$

$$dF_s = -S_s dT - PdV_s - \phi dA_s + \mu_s dn_s \quad (5.2.3c)$$

$$dG_s = -S_s dT + V_s dP + A_s d\phi + \mu_s dn_s \quad (5.2.3d)$$

$$dE'_s = TdS_s - PdV_s + A_s d\phi + \mu_s dn_s \quad (5.2.3e)$$

$$dH'_s = TdS_s + V_s dP - \phi dA_s + \mu_s dn_s \quad (5.2.3f)$$

$$dF'_s = -S_s dT - PdV_s + A_s d\phi + \mu_s dn_s \quad (5.2.3g)$$

$$dG'_s = -S_s dT + V_s dP - \phi dA_s + \mu_s dn_s. \quad (5.2.3h)$$

The above expressions can be doubly differentiated in either order with respect to two different independent variables to produce 48 Maxwell-type relations, which are listed in Table 5.2.I. Only a small fraction of these turn out to be useful; they will be introduced below as needed.

Table 5.2.I Maxwell Relations Based on Eqs. (5.2.3)

From E_s : (T5.2.1)

$$\begin{aligned} \left(\frac{\partial T}{\partial V_s}\right)_{S_s, A_s, n_s} &= -\left(\frac{\partial P}{\partial S_s}\right)_{V_s, A_s, n_s} & \left(\frac{\partial \phi}{\partial V_s}\right)_{S_s, A_s, n_s} &= \left(\frac{\partial P}{\partial A_s}\right)_{S_s, V, n_s} \\ \left(\frac{\partial T}{\partial A_s}\right)_{S_s, V_s, n_s} &= -\left(\frac{\partial \phi}{\partial S_s}\right)_{V_s, A_s, n_s} & \left(\frac{\partial P}{\partial n_s}\right)_{S_s, V_s, A_s} &= -\left(\frac{\partial \mu_s}{\partial V_s}\right)_{S_s, A_s, n_s} \\ \left(\frac{\partial T}{\partial n_s}\right)_{S_s, V_s, A_s} &= \left(\frac{\partial \mu_s}{\partial S_s}\right)_{V_s, A_s, n_s} & \left(\frac{\partial \phi}{\partial n_s}\right)_{S_s, V_s, A_s} &= -\left(\frac{\partial \mu_s}{\partial A_s}\right)_{S_s, V_s, n_s} \end{aligned}$$

From H_s : (T5.2.2)

$$\begin{aligned} \left(\frac{\partial T}{\partial P}\right)_{S_s, \phi, n_s} &= \left(\frac{\partial V_s}{\partial S_s}\right)_{P, \phi, n_s} & \left(\frac{\partial V_s}{\partial \phi}\right)_{S_s, P, n_s} &= \left(\frac{\partial A_s}{\partial P}\right)_{S_s, \phi, n_s} \\ \left(\frac{\partial T}{\partial \phi}\right)_{S_s, P, n_s} &= \left(\frac{\partial A_s}{\partial S_s}\right)_{P, \phi, n_s} & \left(\frac{\partial V_s}{\partial n_s}\right)_{S_s, P, \phi} &= \left(\frac{\partial \mu_s}{\partial P}\right)_{S_s, \phi, n_s} \\ \left(\frac{\partial T}{\partial n_s}\right)_{S_s, P, \phi} &= \left(\frac{\partial \mu_s}{\partial S_s}\right)_{P, \phi, n_s} & \left(\frac{\partial A_s}{\partial n_s}\right)_{S_s, P, \phi} &= \left(\frac{\partial \mu_s}{\partial \phi}\right)_{S_s, P, n_s} \end{aligned}$$

From F_s : (T5.2.3)

$$\begin{aligned} \left(\frac{\partial S_s}{\partial V_s}\right)_{T, A_s, n_s} &= \left(\frac{\partial P}{\partial T}\right)_{V_s, A_s, n_s} & \left(\frac{\partial P}{\partial A_s}\right)_{T, V_s, n_s} &= \left(\frac{\partial \phi}{\partial V_s}\right)_{T, A_s, n_s} \\ \left(\frac{\partial S_s}{\partial A_s}\right)_{T, V_s, n_s} &= \left(\frac{\partial \phi}{\partial T}\right)_{V_s, A_s, n_s} & \left(\frac{\partial P}{\partial n_s}\right)_{T, V_s, A_s} &= -\left(\frac{\partial \mu_s}{\partial V_s}\right)_{T, A_s, n_s} \\ \left(\frac{\partial S_s}{\partial n_s}\right)_{T, V_s, A_s} &= -\left(\frac{\partial \mu_s}{\partial T}\right)_{V_s, A_s, n_s} & \left(\frac{\partial \phi}{\partial n_s}\right)_{T, V_s, A_s} &= -\left(\frac{\partial \mu_s}{\partial A_s}\right)_{T, V_s, n_s} \end{aligned}$$

Continued

Table 5.2.I Maxwell Relations Based on Eqs. (5.2.3)—cont'd**From G_s : (T5.2.4)**

$$\begin{aligned} \left(\frac{\partial S_s}{\partial P}\right)_{T,\phi,n_s} &= -\left(\frac{\partial V_s}{\partial T}\right)_{P,\phi,n_s} & \left(\frac{\partial V_s}{\partial \phi}\right)_{T,P,n_s} &= \left(\frac{\partial A_s}{\partial P}\right)_{T,\phi,n_s} \\ \left(\frac{\partial S_s}{\partial \phi}\right)_{T,P,n_s} &= -\left(\frac{\partial A_s}{\partial T}\right)_{P,\phi,n_s} & \left(\frac{\partial V_s}{\partial n_s}\right)_{T,P,\phi} &= \left(\frac{\partial \mu_s}{\partial P}\right)_{T,\phi,n_s} \\ \left(\frac{\partial S_s}{\partial n_s}\right)_{T,P,\phi} &= -\left(\frac{\partial \mu_s}{\partial T}\right)_{P,\phi,n_s} & \left(\frac{\partial A_s}{\partial n_s}\right)_{T,P,\phi} &= \left(\frac{\partial \mu_s}{\partial \phi}\right)_{T,P,n_s} \end{aligned}$$

From E'_s : (T5.2.5)

$$\begin{aligned} \left(\frac{\partial T}{\partial V_s}\right)_{S_s,\phi,n_s} &= -\left(\frac{\partial P}{\partial S_s}\right)_{V_s,\phi,n_s} & \left(\frac{\partial P}{\partial \phi}\right)_{S_s,V_s,n_s} &= -\left(\frac{\partial A_s}{\partial V_s}\right)_{S_s,\phi,n_s} \\ \left(\frac{\partial T}{\partial \phi}\right)_{S_s,V_s,n_s} &= \left(\frac{\partial A_s}{\partial S_s}\right)_{V_s,\phi,n_s} & \left(\frac{\partial P}{\partial n_s}\right)_{S_s,V_s,\phi} &= -\left(\frac{\partial \mu_s}{\partial V_s}\right)_{S_s,\phi,n_s} \\ \left(\frac{\partial T}{\partial n_s}\right)_{S_s,V_s,\phi} &= \left(\frac{\partial \mu_s}{\partial S_s}\right)_{V_s,\phi,n_s} & \left(\frac{\partial A_s}{\partial n_s}\right)_{S_s,V_s,\phi} &= \left(\frac{\partial \mu_s}{\partial \phi}\right)_{S_s,V_s,n_s} \end{aligned}$$

From H'_s : (T5.2.6)

$$\begin{aligned} \left(\frac{\partial T}{\partial P}\right)_{S_s,A_s,n_s} &= \left(\frac{\partial V_s}{\partial S_s}\right)_{P,A_s,n_s} & \left(\frac{\partial V_s}{\partial A_s}\right)_{S_s,P,n_s} &= -\left(\frac{\partial \phi}{\partial P}\right)_{S_s,A_s,n_s} \\ \left(\frac{\partial T}{\partial A_s}\right)_{S_s,P,n_s} &= -\left(\frac{\partial \phi}{\partial S_s}\right)_{P,A_s,n_s} & \left(\frac{\partial V_s}{\partial n_s}\right)_{S_s,P,A_s} &= \left(\frac{\partial \mu_s}{\partial P}\right)_{S_s,A_s,n_s} \\ \left(\frac{\partial T}{\partial n_s}\right)_{S_s,P,A_s} &= \left(\frac{\partial \mu_s}{\partial S_s}\right)_{P,A_s,n_s} & \left(\frac{\partial \phi}{\partial n_s}\right)_{S_s,P,A_s} &= -\left(\frac{\partial \mu_s}{\partial A_s}\right)_{S_s,P,n_s} \end{aligned}$$

From F'_s : (T5.2.7)

$$\begin{aligned} \left(\frac{\partial S_s}{\partial V_s}\right)_{T,\phi,n_s} &= \left(\frac{\partial P}{\partial T}\right)_{V_s,\phi,n_s} & \left(\frac{\partial P}{\partial \phi}\right)_{T,V_s,n_s} &= -\left(\frac{\partial A_s}{\partial V_s}\right)_{T,\phi,n_s} \\ \left(\frac{\partial S_s}{\partial \phi}\right)_{T,V_s,n_s} &= -\left(\frac{\partial A_s}{\partial T}\right)_{V_s,\phi,n_s} & \left(\frac{\partial P}{\partial n_s}\right)_{T,V_s,\phi} &= -\left(\frac{\partial \mu_s}{\partial V_s}\right)_{T,\phi,n_s} \\ \left(\frac{\partial S_s}{\partial n_s}\right)_{T,V_s,\phi} &= -\left(\frac{\partial \mu_s}{\partial T}\right)_{V_s,\phi,n_s} & \left(\frac{\partial A_s}{\partial n_s}\right)_{T,V_s,\phi} &= \left(\frac{\partial \mu_s}{\partial \phi}\right)_{T,V_s,n_s} \end{aligned}$$

From G'_s : (T5.2.8)

$$\begin{aligned} \left(\frac{\partial S_s}{\partial P}\right)_{T,A_s,n_s} &= -\left(\frac{\partial V_s}{\partial T}\right)_{P,A_s,n_s} & \left(\frac{\partial V_s}{\partial A_s}\right)_{T,P,n_s} &= -\left(\frac{\partial \phi}{\partial P}\right)_{T,A_s,n_s} \\ \left(\frac{\partial S_s}{\partial A_s}\right)_{T,P,n_s} &= \left(\frac{\partial \phi}{\partial T}\right)_{P,A_s,n_s} & \left(\frac{\partial V_s}{\partial n_s}\right)_{T,P,A_s} &= \left(\frac{\partial \mu_s}{\partial P}\right)_{T,A_s,n_s} \\ \left(\frac{\partial S_s}{\partial n_s}\right)_{T,P,A_s} &= -\left(\frac{\partial \mu_s}{\partial T}\right)_{P,A_s,n_s} & \left(\frac{\partial \phi}{\partial n_s}\right)_{T,P,A_s} &= -\left(\frac{\partial \mu_s}{\partial A_s}\right)_{T,P,n_s} \end{aligned}$$

The Gibbs–Duhem Relation as a Basic Expression for Gas Adsorption

We derive here the basic Gibbs–Duhem relation that is needed in our subsequent analysis. For a one-component adsorbate system, the Gibbs free energy assumes the form $G_s = \mu_s(T, P, \phi)n_s$. Note that G_s contains all the intensive variables in its argument. Accordingly, we write

$$dG_s = \mu_s dn_s + n_s d\mu_s \quad (5.2.4a)$$

and

$$dG_s = \mu_s dn_s + n_s \left[(\partial \mu_s / \partial T)_{P, \phi} dT + (\partial \mu_s / \partial P)_{T, \phi} dP + (\partial \mu_s / \partial \phi)_{T, P} d\phi \right], \quad (5.2.4b)$$

which shows how changes in G_s involve alterations in T , P , and ϕ . Equation (5.2.4b) should be compared with Eq. (5.2.3d). Consistency requires that

$$n_s d\mu_s = -S_s dT + V_s dP + A_s d\phi. \quad (5.2.5a)$$

We now define $\Gamma \equiv n_s/A_s$ as the *surface concentration of the adsorbed species*, whence the above equation reads

$$d\mu_s = -\tilde{S}_s dT + \tilde{V}_s dP + (1/\Gamma) d\phi. \quad (5.2.5b)$$

The corresponding equation for the gas phase is given by

$$d\mu_g = -\tilde{S}_g dT + \tilde{V}_g dP. \quad (5.2.6)$$

On equating the two expressions at equilibrium, one obtains the fundamental expression that generalizes the ordinary Clausius–Clapeyron equation:

$$(\tilde{S}_g - \tilde{S}_s) dT - (\tilde{V}_g - \tilde{V}_s) dP + (1/\Gamma) d\phi = 0. \quad (5.2.7)$$

Adsorption Isotherms

We now deal here with the types of experimental data in the literature, by which surface adsorption effects are analyzed. One common experiment involves measuring *adsorption isotherms*. By weighing or by volumetric techniques, one determines as a function of the equilibrium gas pressure the amount of gas held on a given surface at a specified temperature. Usually this quantity varies sigmoidally with rising pressure P , as sketched in Figure 5.2.1 for a variety of temperatures T_i . By standard methods that rely on the *Brunauer, Emmett, Teller isotherm equation*,^{2,7} one can determine the point on the isotherms at which monolayer coverage of the surface is complete; it is usually located fairly close to the knee of the isotherm. From the cross-sectional area of the adsorbate molecules, and from the amount needed for monolayer coverage, one may then ascertain more or less quantitatively the surface area of the adsorbent, A_s .

A second set of measurements involves heats of adsorption by calorimetric techniques under conditions specified below. These heats are reported as a function of the amount of adsorbate held on the surface. For both sets of measurements, the fundamental experimental variable is the surface concentration of adsorbate, $\Gamma \equiv n_s/A_s$.

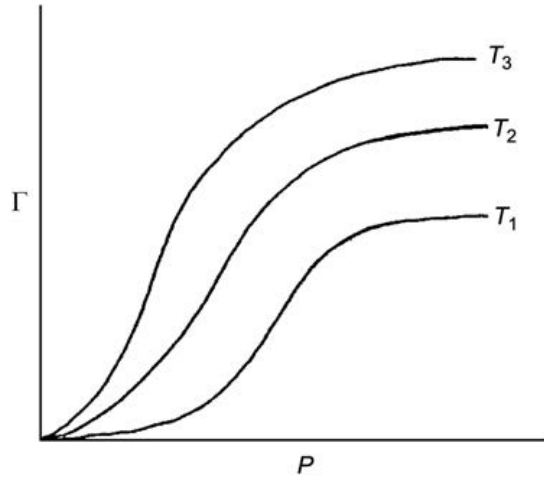


FIGURE 5.2.1

Schematic representation of several experimental isotherms for gases adsorbed on an adsorbent at a set of temperatures $T_1 > T_2 > T_3$.

Adsorption at Constant Temperature

We now deal with Eq. (5.2.7) under a variety of special cases. At constant temperature, one finds

$$d\phi = \Gamma(\tilde{V}_g - \tilde{V}_s)dP \approx \Gamma\tilde{V}_g dP, \quad (5.2.8)$$

where the volume of the adsorbed phase has been neglected compared to that of the gas. For an ideal gas, the above reduces to

$$d\phi = \Gamma(P, T)RT \ln P, \quad (5.2.9)$$

which is known as the (differential form of the) *Gibbs adsorption isotherm equation* at constant temperature. The integrated form of the above expression is

$$\phi(P, T) = RT \int_0^P (\Gamma(P, T)/P) dP, \quad (5.2.10)$$

This relation shows how the two-dimensional pressure may be determined through measurements of Γ at a sequence of equilibrium gas pressures P at a fixed temperature, followed either by graphical or numerical integration, or analytically, by curve fitting procedures.

Adsorption at Constant Spreading Pressures

When ϕ is held constant, Eq. (5.2.7) reduces to

$$\left(\frac{\partial P}{\partial T}\right)_\phi = \frac{\tilde{S}_g - \tilde{S}_s}{\tilde{V}_g - \tilde{V}_s} \approx \frac{\tilde{S}_g - \tilde{S}_s}{\tilde{V}_g}, \quad (5.2.11)$$

where we have again neglected the molar volume of the adsorbate on the right. On introducing the ideal gas law, we obtain

$$\left(\frac{\partial \ln P}{\partial T}\right)_\phi = \frac{\tilde{S}_g - \tilde{S}_s}{RT}, \quad (5.2.12)$$

In principle, by knowing the molar entropy of the perfect gas [Section 2.4], and by measuring the change of equilibrium gas pressure as a function of temperature, one can determine the molar entropy of the adsorbed phase. The difficulty here is that the experiment is to be carried out at constant ϕ , a problematic task. Methods for circumventing this difficulty are shown below. Meanwhile, for completeness, we observe that at equilibrium the chemical potentials of the gas and adsorbate will have to match; then $\tilde{H}_g - \tilde{H}_s = T(\tilde{S}_g - \tilde{S}_s)$, so that we obtain the alternative formulation,

$$\left(\frac{\partial \ln P}{\partial T}\right)_\phi = \frac{\tilde{H}_g - \tilde{H}_s}{RT^2} \equiv \frac{\tilde{Q}_\phi}{RT^2}, \quad (5.2.13)$$

showing that under conditions of constant ϕ , an experimental determination of the left can be correlated with an enthalpy change involving the transfer of 1 mol of gas to the surface; the concomitant “heat of transfer” is designated as shown on the right.

Adsorption at Constant Surface Coverage

Experimentally, it is much simpler to consider changes in adsorption at constant surface coverage rather than at constant spreading pressure. Unfortunately, the mathematical analysis now is also more complicated. When $\Gamma(T, P)$ is held fixed, P and T are no longer independent. We set $dP = (\partial P / \partial T)_\Gamma dT$ and we rewrite Eq. (5.2.7) in the form

$$\left(\frac{\partial \phi}{\partial P}\right)_{\Gamma, T} \left(\frac{\partial P}{\partial T}\right)_\Gamma + \left(\frac{\partial \phi}{\partial T}\right)_{\Gamma, P} = -\Gamma(\tilde{S}_g - \tilde{S}_s) + \Gamma(\tilde{V}_g - \tilde{V}_s) \left(\frac{\partial P}{\partial T}\right)_\Gamma. \quad (5.2.14)$$

On solving for $(\partial P / \partial T)_\Gamma$, we obtain

$$\left(\frac{\partial P}{\partial T}\right)_\Gamma = \frac{(\tilde{S}_g - \tilde{S}_s) + (1/\Gamma)(\partial \phi / \partial T)_{\Gamma, P}}{(\tilde{V}_g - \tilde{V}_s) - (1/\Gamma)(\partial \phi / \partial P)_{\Gamma, T}} = \frac{(\tilde{H}_g - \tilde{H}_s) + (T/\Gamma)(\partial \phi / \partial T)_{\Gamma, P}}{T[(\tilde{V}_g - \tilde{V}_s) - (1/\Gamma)(\partial \phi / \partial P)_{\Gamma, T}]}. \quad (5.2.15)$$

In this rather formidable relation, the derivatives involving ϕ may be inserted from differentiation of the empirical relation, Eq. (5.2.10). However, Eq. (5.2.15) is often simplified by noting that in the original two-dimensional equation of state $\phi = \phi(\Gamma, T)$, the pressure P does not appear explicitly. Therefore, presumably, no significant error is introduced by neglecting this term. When this is done, along with the approximation $\tilde{V}_s \ll \tilde{V}_g = RT/P$, Eq. (5.2.15) reduces to

$$\left(\frac{\partial \ln P}{\partial T}\right)_\Gamma \approx \frac{\tilde{S}_g - \tilde{S}_s}{RT} + \frac{1}{\Gamma RT} \left(\frac{\partial \phi}{\partial T}\right)_{\Gamma, P} = \frac{1}{RT^2} \left[(\tilde{H}_g - \tilde{H}_s) + \frac{T}{\Gamma} \left(\frac{\partial \phi}{\partial T}\right)_{\Gamma, P} \right] \equiv \frac{Q_{st}}{RT^2}, \quad (5.2.16)$$

in which Q_{st} is referred to as the *isosteric heat of adsorption*. The left-hand side is found by taking isotherms at a series of closely spaced temperatures and noting the change in equilibrium gas pressure

P at fixed surface coverage Γ . \tilde{S}_g and \tilde{H}_g may be determined as shown in Chapter 1; $(\partial\phi/\partial T)_{\Gamma,P}$ is found either through the two-dimensional equation of state, or via Eqs. (5.2.8) and (5.2.10). Then \tilde{S}_s or \tilde{H}_s is accessible for any particular measured Γ value.

Differential Entropies of Adsorption

So far we have dealt with molar quantities such as \tilde{S}_s or \tilde{H}_s . However, considerable interest also attaches to the corresponding differential quantities $\partial S_s/\partial n_s$ and $\partial H_s/\partial n_s$ that are to be determined under various conditions.

A systematic analysis requires the use of four Maxwell relations:

$$(\partial S_s/\partial n_s)_{T,V_s,A_s} = -(\partial \mu_s/\partial T)_{V_s,\Gamma} \quad (5.2.17a)$$

$$(\partial S_s/\partial n_s)_{T,P,\phi} = -(\partial \mu_s/\partial T)_{P,\phi,n_s} \quad (5.2.17b)$$

$$(\partial S_s/\partial n_s)_{T,V_s,\phi} = -(\partial \mu_s/\partial T)_{V_s,\phi,n_s} \quad (5.2.17c)$$

$$(\partial S_s/\partial n_s)_{T,P,A_s} = -(\partial \mu_s/\partial T)_{P,\Gamma}. \quad (5.2.17d)$$

These relations were taken from sets III, IV, VII, and VIII of Table 5.2.I. One may now determine the right-hand side of the above equations using Eq. (5.2.5b). Due attention should be paid to the various experimental quantities that are to be held fixed in the partial differentiations. One finds

$$(\partial S_s/\partial n_s)_{T,V_s,A_s} = \tilde{S}_s - \tilde{V}_s(\partial P/\partial T)_{V_s,\Gamma} - (1/\Gamma)(\partial\phi/\partial T)_{V_s,\Gamma} \quad (5.2.18a)$$

$$(\partial S_s/\partial n_s)_{T,P,\phi} = \tilde{S}_s \quad (5.2.18b)$$

$$(\partial S_s/\partial n_s)_{T,V_s,\phi} = \tilde{S}_s - \tilde{V}_s(\partial P/\partial T)_{V_s,\phi,n_s} \quad (5.2.18c)$$

$$(\partial S_s/\partial n_s)_{T,P,A_s} = \tilde{S}_s - (1/\Gamma)(\partial\phi/\partial T)_{P,\Gamma}. \quad (5.2.18d)$$

The above expressions furnish four interrelations between the molar entropy \tilde{S}_s and the various differential entropies $\partial S_s/\partial n_s$. Note that it is only when the three intensive quantities T , P , and ϕ are held fixed that the molar entropy of the adsorbed phase is equal to its partial molal counterpart. The terms involving \tilde{V}_s are usually small and are generally neglected.

Other Partial Molal Quantities for the Adsorbate

Other interrelations between molar and differential quantities for adsorbates are furnished by use of Eqs. (5.2.2) and (5.2.3):

$$(\partial F_s/\partial n_s)_{T,V_s,A_s} = (\partial E_s/\partial n_s)_{T,V_s,A_s} - T(\partial S_s/\partial n_s)_{T,V_s,A_s} = \mu_s = \tilde{H}_s - T\tilde{S}_s \quad (5.2.19a)$$

$$(\partial G_s/\partial n_s)_{T,P,\phi} = (\partial H_s/\partial n_s)_{T,P,\phi} - T(\partial S_s/\partial n_s)_{T,P,\phi} = \mu_s = \tilde{H}_s - T\tilde{S}_s \quad (5.2.19b)$$

$$(\partial F'_s/\partial n_s)_{T,V_s,\phi} = (\partial E'_s/\partial n_s)_{T,V_s,\phi} - T(\partial S_s/\partial n_s)_{T,V_s,\phi} = \mu_s = \tilde{H}_s - T\tilde{S}_s \quad (5.2.19c)$$

$$(\partial G'_s/\partial n_s)_{T,P,A_s} = (\partial H'_s/\partial n_s)_{T,P,A_s} - T(\partial S_s/\partial n_s)_{T,P,A_s} = \mu_s = \tilde{H}_s - T\tilde{S}_s. \quad (5.2.19d)$$

The right-hand side was determined using Eqs. (5.2.3c), (5.2.3d), (5.2.3g) and (5.2.3h).

Next, eliminate the differential entropies between Eqs. (5.2.18) and (5.2.19). Then

$$(\partial E_s / \partial n_s)_{T, V_s, A_s} = \tilde{H}_s - T \tilde{V}_s (\partial P / \partial T)_{V_s, \Gamma} - (T / \Gamma) (\partial \phi / \partial T)_{V_s, \Gamma} \quad (5.2.20a)$$

$$(\partial H_s / \partial n_s)_{T, P, \phi} = \tilde{H}_s \quad (5.2.20b)$$

$$(\partial E'_s / \partial n_s)_{T, V_s, \phi} = \tilde{H}_s - T \tilde{V}_s (\partial P / \partial T)_{V_s, \phi, n_s} \quad (5.2.20c)$$

$$(\partial H'_s / \partial n_s)_{T, P, A_s} = \tilde{H}_s - (T / \Gamma) (\partial \phi / \partial T)_{P, \Gamma}. \quad (5.2.20d)$$

The above equations again correlate partial molal and molar energies and enthalpies; only when all intensive variables are held fixed, is the partial molal and molar enthalpy the same. In most cases, one may drop the term involving \tilde{V}_s . One may also use Eqs. (5.2.2) to access other thermodynamic functions of interest in terms of differential quantities.

As a special application of the above, we introduce Eq. (5.2.20d) into Eq. (5.2.16) to obtain

$$\left(\frac{\partial \ln P}{\partial T} \right)_{\Gamma} = \frac{\tilde{H}_g - (\partial H'_s / \partial n_s)_{T, P, A_s}}{RT^2}, \quad (5.2.21)$$

which relates the quantity on the left, that can be readily determined experimentally by taking isotherms at narrow temperature intervals, to the differential enthalpy of the adsorbate.

References and Exercises

- 5.2.1.** Consult T.L. Hill, *Thermodynamics of Small Systems* (Benjamin, New York, 1963).
- 5.2.2.** Consult S. Brunauer, *The Adsorption of Gases and Vapors* (University Press, Princeton, New Jersey, 1945).
- 5.2.3.** The two-dimensional equation of state may be put in the following virial form:
 $\phi = RT + [n_s / A_s + n_s^2 C_2(T) / A_s^2 + n_s^3 C_3(T) / A_s^3 + \dots]$. Derive the corresponding isotherm equation in the form $P = P(T, \Gamma)$. Derive expressions for the molar enthalpy and entropy of the adsorbate, assuming that the gas phase is ideal.
- 5.2.4.** The *Langmuir adsorption isotherm* is represented by $P = K\Gamma / (\Gamma_m - \Gamma)$, where K is a function of T only, and Γ_m represents the maximum concentration of adsorbed species that can be accommodated as a monolayer on the surface. Derive the corresponding two-dimensional equation of state. Determine the molar enthalpy and entropy of the adsorbate, using the perfect gas approximation for the gaseous phase.
- 5.2.5.** Repeat Exercise 4 for the isotherm equation $P = K(T)(\Gamma / (\Gamma_m - \Gamma)) \exp(C / \Gamma_m RT)$, where the symbols were defined as above, and where C is a constant.
- 5.2.6.** In the text, the chemical potential of the adsorbed species was written as $G_s = C_s n_s$. Explain carefully whether it is appropriate to introduce the defining relation as $G'_s = \mu_s n_s$.
- 5.2.7.** Multilayer adsorption isotherms are usually analyzed in terms of the *Brunauer, Emmett, Teller equation* $\Gamma / \Gamma_m = cx / (1 - x)(1 - x + cx)$, where $x \equiv P / P_0$, where P_0 is the saturation vapor pressure of the liquid; c is a parameter, and the other symbols have been defined earlier. Find the equation for the spreading pressure for $x < 1$. Sketch plots of Γ / Γ_m and of ϕ vs x .

5.3 Heats of Adsorption

Aside from adsorption isotherm data, one can use calorimetric techniques to obtain information on adsorbates. The experimental techniques are now more involved, but they do supply direct information on the heats liberated during the adsorption process. Here the use of partial molal quantities is imperative since increments of the heats of adsorption diminish with successive amounts of gas transferred to the adsorbed phase. Here we follow the systematic treatment furnished by Clark.¹

Heats of Adsorption

We begin by applying the first law to the combination of adsorbed and gas phases:

$$\delta Q = dE_s + dE_g + PdV_g + PdV_s + \phi dA_s. \quad (5.3.1)$$

Before considering various special cases, we introduce the *differential heat of adsorption* \bar{Q} through the definition $\delta Q \equiv -\bar{Q}dn_s$.

The following particular experimental conditions are frequently reported in the literature:

(i) T, V_g, V_s, A_s constant: Eq. (5.3.1) now assumes the form

$$\delta Q|_{T,V_g} = dE_g + dE_s. \quad (5.3.2a)$$

The energy of the gas phase may be written in natural coordinates as $E_g = E_g(S_g, V_g, n_g)$ by use of the relation $S_g = S_g(T, V_g, n_g)$ we can reexpress the energy in unnatural coordinates $E_g = E_g(T, V_g, n_g)$ as we did in Section 1.12. Under present constraints, E_g varies only with n_g ; thus,

$$dE_g|_{T,V_g} = (\partial E_g / \partial n_g)_{T,V_g} dn_g = -(\partial E_g / \partial n_s)_{T,V_g} dn_s, \quad (5.3.2b)$$

where for the closed system normally employed in calorimetric measurements, we have set $dn_s = -dn_g$. Precisely, the same analysis can be carried out for the adsorbed phase where, in unnatural coordinates, we deal with the function $E_s = E_s(T, V_s, A_s, n_s)$ under the prescribed condition E_s varies with n_s alone. Thus,

$$dE_s|_{T,V_s,A_s} = (\partial E_s / \partial n_s)_{T,V_s,A_s} dn_s. \quad (5.3.2c)$$

Putting these results into Eq. (5.3.1) yields

$$-\bar{Q}dn_s = -(\partial E_g / \partial n_g)_{T,V_g} dn_s + (\partial E_s / \partial n_s)_{T,V_s,A_s} dn_s. \quad (5.3.3a)$$

Next, we set $E = \tilde{E}_g n_g$ and $E_s = \tilde{E}_s n_s$ and note that for an ideal gas, \tilde{E}_g is independent of V_g or n_g . Then Eq. (5.3.3a) reduces to

$$-\bar{Q}_d = \tilde{E}_g - (\partial E_s / \partial n_s)_{T,V_s,A_s} = \tilde{E}_g - \tilde{E}_s - n_s (\partial \tilde{E}_s / \partial n_s)_{T,V_s,A_s} = \tilde{E}_g - \tilde{E}_s - \Gamma (\partial \tilde{E}_s / \partial \Gamma)_{T,V_s,A_s}. \quad (5.3.3b)$$

The above quantity is known as the *differential heat of adsorption*. Although the measurement is simple, since volumes and surface areas are kept fixed, the interpretation of the experimental measurements is somewhat more involved than for several of the cases cited below.

(ii) T, P, ϕ constant: We rewrite Eq. (5.3.1) as

$$\mathfrak{d}Q_e = d(E_g + PV_g) + d(E_s + PV_s + \phi A_s) = dH_g + dH_s \equiv -\bar{Q}_e dn_s. \quad (5.3.4a)$$

The above relation is clearly of the same form as Eq. (5.3.2a); moreover, T, P , and ϕ are the appropriate unnatural coordinates for H_g and for H_s ; also, because $(\partial H_g / \partial n_s)(\partial n_s / \partial n_g) = -\tilde{H}_g$, we deduce that

$$\bar{Q}_e = (\partial H_g / \partial n_g)_{T,P} - (\partial H_s / \partial n_s)_{T,P,\phi} = \tilde{H}_g - \tilde{H}_s - n_s (\partial \tilde{H}_s / \partial n_s)_{T,P,\phi}, \quad (5.3.4b)$$

which is known as the *equilibrium heat of adsorption*. Note that when all intensive variables are held fixed, the partial molal and molar enthalpies of the gas and adsorbate phases are identical. Obviously, this is the simplest relationship involving the enthalpy of the adsorbed phase, but experimentally it is difficult to operate under conditions where the spreading pressure must be held fixed.

(iii) T, V_g, V_s, ϕ constant: Here we rewrite Eq. (5.3.1) in the form

$$\mathfrak{d}Q_e = dE_g + d(E_s + \phi A_s) = dE_g + dE'_s \equiv -\bar{Q}' dn_s, \quad (5.3.5a)$$

so that

$$-\bar{Q}' = (\partial E_g / \partial n_g)_{T,V_g} - (\partial E'_s / \partial n_s)_{T,V_s,\phi} = \tilde{E}_g - \tilde{E}'_s - n_s (\partial \tilde{E}'_s / \partial n_s)_{T,V_s,\phi}. \quad (5.3.5b)$$

This quantity has not been assigned a name.

(iv) T, P, A_s constant. Here we put Eq. (5.3.1) in the form

$$\mathfrak{d}Q_{st} = d(E_g + PV_g) + d(E_s + PV_s) = dH_g + dH'_s \equiv -\bar{Q}_{st} dn_s, \quad (5.3.6a)$$

whence

$$\bar{Q}_{st} = (\partial H_g / \partial n_g)_{T,P} - (\partial H'_s / \partial n_s)_{T,P,A_s} = \tilde{H}_g - \tilde{H}'_s - \Gamma (\partial H'_s / \partial \Gamma)_{T,P,A_s}. \quad (5.3.6b)$$

This quantity is known as the *isosteric (differential) heat of adsorption*. The experimental requirements are easily satisfied but the interpretation of the results is now more involved than for Eq. (5.3.4b). Incidentally, here and below, the quantity \tilde{H}'_s may be experimentally determined as shown below in Eq. (5.3.17).

(v) T, A_s constant: Under these conditions, Eq. (5.3.1) reads

$$\mathfrak{d}Q_{th} = dE_g + dE_s + PdV_g + PdV_s \equiv \bar{Q}_{th} dn_s. \quad (5.3.7)$$

We must now introduce the entropy of the adsorbate, $S_s = S_s(T, V_s, A_s, n_s)$ to substitute for the entropy in $E_s = E_s(S_s, V_s, A_s, n_s)$ so that at constant T, A_s

$$dE_s|_{T,A_s} = T(\partial S_s / \partial V_s)_{T,A_s,n_s} dV_s + T(\partial S_s / \partial n_s)_{T,V_s,A_s} dn_s - PdV_s + \mu_s dn_s. \quad (5.3.8a)$$

Now introduce Maxwell's relation $(\partial S_s/\partial V_s)_{T,\Gamma} = (\partial P/\partial T)_{V_s,\Gamma}$ as read off from Part (T5.2.3) of Table 5.2.I, and set $\mu_s + T(\partial S_s/\partial V_s)_{T,V_s,A_s} = (\partial E_s/\partial n_s)_{T,V_s,A_s}$. Here energy is a function of state; thus, $dE_s|_{T,V_s,A_s} = (\partial E_s/\partial n_s)_{T,V_s,A_s} dn_s$, and this quantity must match the coefficient of dn_s in Eq. (5.3.8a). Under present restrictions, we then find

$$dE_s|_{T,A_s} = \left[T(\partial P/\partial T)_{V_s,\Gamma} - P \right] dV_s + (\partial E_s/\partial n_s)_{T,V_s,A_s} dn_s. \quad (5.3.8b)$$

By an exactly analogous procedure, one obtains $(dn_s = -dn_g)$.

$$dE_g|_{T,A_s} = \left[T(\partial P/\partial T)_{V_g,n_g} - P \right] dV_g + (\partial E_g/\partial n_g)_{T,V_g} dn_g. \quad (5.3.8c)$$

One should note that Eq. (5.3.8c) represents an extension of the ordinary caloric equation of state, Eq. (1.12.8); the above relation applies when mole numbers are allowed to vary. Equation (5.3.7), together with Eqs. (5.3.8b) and (5.3.8c) and with $dn_s = -dn_g$ may now be rewritten as

$$\begin{aligned} \bar{Q}_{th} = & (\partial E_g/\partial n_g)_{T,V_g} - (\partial E_s/\partial n_s)_{T,V_s,A_s} + T(\partial P/\partial T)_{V_g,n_g} (\partial V_g/\partial n_g)_{T,P} \\ & - T(\partial P/\partial T)_{V_s,\Gamma} (\partial V_s/\partial n_s)_{T,A_s}, \end{aligned} \quad (5.3.9a)$$

which is known as the *isothermal heat of adsorption*. It is conventional to introduce the perfect gas law and to ignore terms involving V_s . Equation (5.3.9a) then reduces to

$$\begin{aligned} \bar{Q}_{th} \approx & \tilde{E}_g - (\partial E_s/\partial n_s)_{T,V_s,A_s} + P(\partial V_g/\partial n_g)_{T,P} \\ = & \tilde{H}_g - \tilde{E}_s - \Gamma(\partial \tilde{E}_s/\partial \Gamma)_{T,V_s,A_s}. \end{aligned} \quad (5.3.9b)$$

The above equation shows again that under readily accessible conditions, the interpretation of the experimental results is more complicated than for case (ii). One should also compare the present results to those displayed in case (iv).

- (vi) *Adiabatic conditions, A_s constant.* Here one must introduce the thermal properties of the calorimeter, denoted by the subscript c, since the measurements depend on the rise of the temperature of the entire system during the adsorption process. It is also simpler to adopt P rather than V as the independent variable. We thus rewrite Eq. (5.3.1) in the following form:

$$dE_c + dE_g + dE_s + d(PV_g) - V_g dP + d(PV_s) - V_s dP = 0, \quad (5.3.10a)$$

or as

$$dH_c + dH_g + dH'_s - V_g dP - V_s dP = 0, \quad (5.3.10b)$$

where the distinction between the energy and enthalpy of the calorimeter has been ignored. We next write

$$dH_c = C_{P,c} dT + (\partial H_c/\partial P)_T dP, \quad (5.3.11a)$$

and we also set

$$\begin{aligned} dH_g &= T(\partial S_g/\partial T)_{P,n_g} dT + T(\partial S_g/\partial P)_{T,n_g} dP + T(\partial S_g/\partial n_g)_{T,P} dn_g + V_g dP + \mu_g dn_g \\ &= C_{P,g} dT + \left[V_g - T(\partial V_g/\partial T)_{P,n_g} \right] dP + (\partial H_g/\partial n_g)_{T,P} dn_g. \end{aligned} \quad (5.3.11b)$$

In the preceding, we have eliminated the partial entropy derivatives via the appropriate Maxwell relation and by use of the expression $\mu_g = \bar{H}_g - T\bar{S}_g$. Equation (5.3.11b) follows from Eq. (1.12.11).

An analogous expression holds for the adsorbed phase, involving the function dH'_s , with A_s held fixed. On inserting Eqs. (5.3.11a) and (5.3.11b) and its adsorbate counterpart into Eq. (5.3.10b), one finds

$$\begin{aligned} [C_{P,c} + C_{P,g} + C_{P,s}](\partial T/\partial n_s)_{S,A_s} &\equiv \bar{Q}_{ad} = - \left[(\partial H_c/\partial P)_T - T(\partial V_g/\partial T)_{P,n_g} \right. \\ &\quad \left. - T(\partial V_s/\partial T)_{P,A_s,n_s} \right] (\partial P/\partial n_s)_{S,A_s} \\ &\quad + (\partial H_g/\partial n_g)_{T,P} - (dH'_s/\partial n_s)_{T,P,A_s}, \end{aligned} \quad (5.3.12a)$$

where \bar{Q}_{ad} is termed the *differential adiabatic heat of adsorption*. Ordinarily one may ignore the variation of H_c with P , neglect terms in V_s , and use the perfect gas approximation in the adiabatic limit. In that case, the above reduces to

$$\bar{Q}_{ad} \approx \bar{H}_g - \bar{H}'_s - \Gamma \left(\partial \tilde{H}'_s / \partial \Gamma \right)_{T,P,A_s} - RT/V^{\gamma-1}, \quad (5.3.12b)$$

where the last term is sometimes omitted as well. Note that the adiabatic experiment is a measure of \tilde{H}'_s , not of \bar{H}_s .

In summary, the various calorimetric measurements correspond to distinct differential energies or entropies or to their molar counterparts. The measurements differ in the experimental quantities that are held fixed during the measurements. In cases where ϕ is held constant, the experiments are not readily carried out; then further manipulations are required to cast Eqs. (5.3.4) and (5.3.5) into a useful form for experimentalists; see the queries below. In any case, it is important to examine closely the various assumed experimental constraints to obtain the correct interpretation of the experimental measurements.

Energetics of the Adsorbed Phase at Constant n_s

We briefly consider how the energy of the adsorbed phase varies with temperature, pressure, and surface area at a constant density n_s of the adsorbate. For this purpose, we again express E_s in unnatural coordinates by using the relations $S_s = S_s(T, P, A_s)$ and $V_s = V_s(T, P, A_s)$ at constant n_s ; this allows us to write

$$\begin{aligned} dE_s &= \left[T(\partial S_s/\partial T)_{P,\Gamma} - P(\partial V_s/\partial T)_{P,\Gamma} \right] dT + \left[T(\partial S_s/\partial P)_{T,\Gamma} - P(\partial V_s/\partial P)_{T,\Gamma} \right] dP \\ &\quad + \left[-\phi + T(\partial S_s/\partial A_s)_{T,P,n_s} - P(\partial V_s/\partial A_s)_{T,P,n_s} \right] dA_s. \end{aligned} \quad (5.3.13)$$

The various terms are interpreted as follows: $T(\partial S_s/\partial T)_{P,\Gamma}$ represents the heat capacity, $C_{P,\Gamma}$, of the adsorbate at constant pressure and surface occupancy Γ . The second term represents the mechanical work involved in the expansion of V_s on heating; here the coefficient of expansion is

relevant: $\alpha_{P,\Gamma} \equiv V_s^{-1}(\partial V_s/\partial T)_{P,\Gamma}$. In the third term, we invoke the Maxwell relation that is specified in Entry (T5.2.8) of Table 5.2.I: $T(\partial S_s/\partial P)_{T,\Gamma} = -T(\partial V_s/\partial T)_{P,\Gamma} = -TV_s\alpha_{P,\Gamma}$, which again relates to mechanical work associated with the alteration of surface phase volume induced by pressure changes. The fourth term describes the contraction in volume of the surface phase due to the application of pressure. This effect is described by the isothermal compressibility $\beta_{T,\Gamma} \equiv -V_s^{-1}(\partial V_s/\partial P)_{T,\Gamma}$. The product $-\phi dA_s$ obviously deals with the work of expanding the surface area. The sixth term is dealt with by use of the Maxwell relation from Table T5.2.8: $T(\partial S_s/\partial A_s)_{T,P,n_s} = T(\partial \phi/\partial T)_{P,\Gamma}$, which relates to the temperature coefficient of the surface tension. We may therefore recast the above equation in the form

$$dE_s = (C_{P,\Gamma} - PV_s\alpha_{P,\Gamma})dT + (-TV_s\alpha_{P,\Gamma} - PV_s\beta_{T,\Gamma})dP + \left[-\phi + T(\partial \phi/\partial T)_{P,\Gamma} - P(\partial V_s/\partial A_s)_{T,P,n_s} \right] dA_s. \quad (5.3.14)$$

The above is considerably simplified under several conditions. If T and P are held fixed and the term in V_s is neglected, we obtain for the energy per unit cross-sectional area the expression

$$e_s = -\phi + T(\partial \phi/\partial T)_{P,\Gamma}. \quad (5.3.15)$$

If, on the other hand, one imposes conditions of constant P and A_s , and if terms in V_s are neglected, Eq. (5.3.13) reduces to

$$(\partial E_s/\partial T)_{P,\Gamma} = T(\partial S_s/\partial T)_{P,\Gamma} = C_{P,\Gamma}, \quad (5.3.16)$$

which involves the heat capacity. The above provides another route to the determination of entropies of the adsorbed phase. The equation also determines the energy E_s . In the same vein, from Eq. (5.2.3), one obtains at constant P

$$dH'_s|_{P,\Gamma} = T(\partial S_s/\partial T)_{P,\Gamma}dT|_{P,\Gamma} = C_{P,\Gamma}dT|_{P,\Gamma}, \quad (5.3.17)$$

which is frequently used to determine H'_s since the constraints are readily applied experimentally.

SUMMARY

Summarizing, we attempted to provide a systematic account of the thermodynamic properties of the adsorbed phase. The Gibbs adsorption equation, as an extension of the Clausius–Clapeyron equation, has played a key role in linking experimental isotherm data to the determination of molar or differential entropies and enthalpies. Similarly, calorimetric measurements can be applied to obtain the same type of information.

Lastly, a reminder: an alternative approach treatment, based on order–disorder theory, was provided in Section 3.10.

Reference and Exercises

5.3.1. A. Clark, *The Theory of Adsorption and Catalysis*, (Academic Press, New York, 1970) Chapter 1.

5.3.2. Rework Eqs. (5.3.4) and (5.3.5) to reexpress the heats in terms of experimental conditions under which Γ rather than ϕ is held fixed.

- 5.3.3.** The two-dimensional analog of the van der Waals equation of state has the form $(\phi + an_s/A_s)(A_s/n_s - b) = k_B T$, where a and b are the parameters and k_B is the Boltzmann's constant. Obtain the corresponding isotherm equation and determine the molar enthalpy and entropy for the case where the bulk gas is ideal. Find the various heats of adsorption and the differential enthalpies and entropies.
- 5.3.4.** For an isotherm equation of the form $P = [c\Gamma/(1 - b\Gamma)]\exp[c\Gamma/(1 - b\Gamma)]$, where c and b are parameters, find the corresponding equation of state of the adsorbed phase and determine the molal entropy and enthalpy of the adsorbed phase relative to $\Gamma = 1$.
- 5.3.5.** Given the two-dimensional equation of state $\phi = RT\Gamma/(1 - b\Gamma) + a\Gamma^2$, where a and b are temperature-independent parameters, determine the corresponding adsorption isotherm. What is the three-dimensional analog of this equation of state?
- 5.3.6.** Verify the following relations:
- (a) $(\partial S_s/\partial A_s)_{T,P,n_s} = [\partial(S_s/n_s)/\partial(1/\Gamma)]_{T,P} = -\Gamma^2((\partial S_s/n_s)/\partial\Gamma)_{T,P} = (\partial\phi/\partial T)_{P,\Gamma}$
 - (b) $(\partial S_s/\partial n_s)_{T,P,A_s} = (\partial\mu/\partial T)_{P,\Gamma}$
 - (c) $(\partial\phi/\partial n_s)_{T,P,A_s} = 1/A_s(\partial\phi/\partial\Gamma)_{T,P} = -(\partial\mu_s/\partial A_s)_{T,P,n_s} = -(1/n_s)[\partial\mu_s/\partial(1/\Gamma)]_{T,P}$
 - (d) $\Gamma^2(\partial\mu_s/\partial\Gamma)_{T,P} = \Gamma(\partial\phi/\partial\Gamma)_{T,P} = (\partial\phi/\partial\ln\Gamma)_{T,P}$.

Are any of the above relations useful?

5.4 Surface vs Bulk Effects: Thermodynamics of Self-Assembly

Hitherto we studied properties of material adsorbed on an inert substrate that remained entirely passive; it merely provided a support for the deposition of a quasi-two-dimensional adsorbed layer whose properties were of interest. We now study the characteristics of surfaces that envelop the bulk material, and correlate the surface properties with those of the bulk. These surface effects obviously become prominent in materials with very small physical dimensions, though still very large on the atomic scale. Whereas earlier the surface area could be varied at will through control of the extent of subdivision of the solid, we are now constrained: the physical extension of the surface is directly linked to that of the bulk, as, for example, in tiny spherical bubbles of radius R , whose surface areas and bulk volumes are governed by R^2 and R^3 , respectively.

For illustrative purposes, consider a semi-infinite rectangular block with a very thin surface layer of area A_s that separates the bulk from an inert gas phase. At equilibrium, the pressure P is uniform perpendicular to the surface layer; the lateral two-dimensional spreading pressure ϕ within the surface layer is also constant. The surface region comprises a volume $V_s = A_s \tau$ where τ is the thickness of the surface layer. As the pressure on the block is decreased, its volume increases; the element of work performed in slightly changing the surface volume is $dW_s = -P(A_s d\tau + \tau dA_s)$; however, the lateral film enlargement is counteracted by the internal two-dimensional spreading pressure ϕ that resists this process (Eq. (1.5.8)). This lateral effect contributes a term $dW_b = \phi dA_s$ to the work, for a total

$$dW = -P(\tau - \phi)dA_s - PA_s d\tau = -PdV_s + \phi dA_s. \quad (5.4.1)$$

Note the change in sign for this surface work term relative to that displayed in Eq. (5.2.1); work must be expended to enlarge the surface area.

Pressures on Curved Surfaces

We study properties of curved surface films by following the procedure of Levine.¹ Examine the two conical sections shown in Figure 5.4.1 that form part of a sphere; an inner layer a is surrounded by an outer layer b of different composition. We are interested in the properties of the curved interfacial layer between the two phases. On the left we show material a being forced reversibly at pressure P_a through the inlet at the bottom, while material b is forced out against the resisting pressure P_b through the upper channel. Because of the curved configuration, the change in volume of the two individual phases, dV_a and dV_b , will be different, while in the indicated configuration of the setup, the total volume $V_t = V_a + V_b$ remains fixed. In the above process, the curved interface moves upward, thereby expanding the area A_s of the interface. Clearly, work must be done on the system to increase this area, which means that the pressure exerted at the bottom must exceed that at the top. Thus, when $P_a > P_b$, $dA_s > 0$.

The element of work involved in reversibly enlarging the surface area of the system at constant temperature is given by

$$\delta W = -P_a dV_a - P_b dV_b + \phi dA_s; \quad (5.4.2)$$

we neglect here the small contribution of the interface volume.

Next, we investigate a similar setup in the configuration of Figure 5.4.1(b), in which the applied pressure, P_b , is uniformly and reversibly exerted on the piston in channel B. Now there is a change in total volume, namely $-dV_t$. The work exerted in this infinitesimal process is

$$\delta W = -P_b dV_t = -P_b (dV_a + dV_b). \quad (5.4.3)$$

Arrange matters so that the same amount of work is expended in the two cases. On equating Eq. (5.4.2) with Eq. (5.4.3), we obtain

$$P_a - P_b = \phi (dA_s / dV_a). \quad (5.4.4)$$

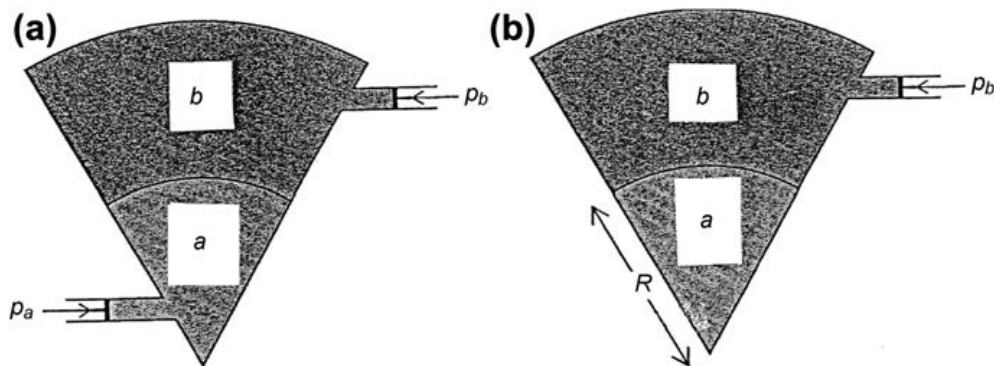


FIGURE 5.4.1

A two-phase system separated by a curved interface, with appropriate inlets and outlets.

After Levine, *loc. cit.*

If the interface is spherical in shape, we may write $V_a = 4\pi r^3/3$ and $A_s = 4\pi r^2$, so that $dV_a = 4\pi r^2 dr$ and $dA_s = 8\pi r dr$, where r is the radius shown in Figure 5.4.1(b). Thus, $dA_s/dV_a = 2/r$, which leads to the fundamental relation

$$P_a - P_b = -2\phi/r. \quad (5.4.5a)$$

For nonspherical surfaces, the pressure difference involves more complicated expressions; for example, for elliptical surfaces with principal radii of curvature r_1 and r_2 , one obtains

$$P_a - P_b = \phi(1/r_1 + 1/r_2). \quad (5.4.5b)$$

Note that the surface tension ϕ can be determined if the equilibrium pressures can be measured experimentally.

Vapor Pressure of Small Drops

We compare the vapor pressure of a small droplet a of radius r with that of a large mass of the same material, b , both at equilibrium with vapor at pressure P . Let the pressures inside these two phases be specified by P_a and P_b . Then on account of Eq. (5.4.5a), we find that

$$P_b = P; \quad P = P_a - 2\phi/r, \quad (5.4.6)$$

Thus, because of surface tension effects, the pressure inside a small droplet is greater than that of the bulk phase. Assuming the material to be incompressible, the corresponding change of chemical potential at fixed T is given by

$$\mu_a - \mu_b = \tilde{V}(P_a - P_b) = 2\phi\tilde{V}/r. \quad (5.4.7)$$

If the vapor phase consists of an ideal gas, we may eliminate the chemical potentials via Eq. (2.4.15) to find

$$\ln(P_a/P_b) = 2\phi\tilde{V}/rRT. \quad (5.4.8)$$

Lastly, setting P_b equal to the bulk vapor pressure P_0 , and dropping the subscript a we find, on expanding the exponential term to first order in ϕ

$$P = P_0(1 + 2\phi M/\rho rRT), \quad (5.4.9)$$

where M is the gram-molecular mass and ρ is the density of the material. This relation shows explicitly the effect that a reduction in radius of a bubble has on raising its vapor pressure. This finding is particularly important in considering the environmental impact of tiny mercury droplets.

Functions of State for Surface Phases

Functions of state for surface phases of the type under consideration are handled in a manner analogous to those of the bulk and will only be studied cursorily. In view of the expression (5.4.1) for the element of reversible work, we may write

$$dE_s = TdS_s - PdV_s + \phi dA_s + \sum_i \mu_{is} dn_{is} \quad (5.4.10)$$

for the energy of the surface phase. Here it is assumed that V_s and A_s may be altered independently, as by a change in thickness of the surface layer. Where this is not the case, one must combine the two terms via the relation $dV_s = q_s dA_s$, where q_s is the factor that depends on the geometric configuration of the material. By use of standard Legendre transforms, we find

$$dG'_s = -S_s dT + V_s dP + \phi dA_s + \sum_i \mu_{is} dn_{is} \quad (5.4.11)$$

for the differential of the (nonstandard) Gibbs free energy considered as a function of T , P , A_s , and n_s . This function of state is of immediate interest because experimentally one can control the surface extension, A_s , by adjustment of the bulk volume, or surface thickness. We now define an enthalpy $H'_s(S_s, P, A_s, n_s)$ for the surface phase, whose differential is given by

$$dH'_s = T dS_s + V_s dP + \phi dA_s + \sum_i \mu_{is} dn_{is}, \quad (5.4.12)$$

which is consistent with the relation

$$G'_s = H'_s - TS_s. \quad (5.4.13)$$

By contrast, the surface analog to dG for the bulk phase is specified by

$$dG_s = -S_s dT + V_s dP - A_s d\phi + \sum_i \mu_{is} dn_{is}, \quad (5.4.14)$$

in which all the independent variables are intensive quantities, but which is experimentally harder to handle since surface pressure measurements are not necessarily easy.

We now compare Eq. (5.4.14) with the relation $dG_s = \sum_i \mu_{is} dn_{is} + \sum_i n_{is} d\mu_{is}$ to find

$$-S_s dT + V_s dP - A_s d\phi - \sum_i n_{is} d\mu_{is} = 0. \quad (5.4.15)$$

For a closed system, we obtain from Eq. (5.4.11) the relation

$$\left(\frac{\partial G'_s}{\partial T} \right)_{A_s, P, n_{is}} = -S_s, \quad (5.4.16)$$

whereas from Eq. (5.4.14), we also find

$$(\partial G_s / \partial T)_{P, \phi, n_{is}} = -S_s, \quad (5.4.17)$$

as well as

$$(\partial G_s / \partial \phi)_{T, P, n_{is}} = -A_s, \quad (5.4.18)$$

and

$$(\partial G_s / \partial n_{is})_{T, P, \phi, n_{is \neq is}} = \mu_{is}. \quad (5.4.19)$$

If we introduce Eq. (5.4.16) into Eq. (5.4.13), we obtain

$$G'_s - T \left(\frac{\partial G'_s}{\partial T} \right)_{A_s, V_s} = H'_s, \quad (5.4.20)$$

which is an adaptation of the conventional Gibbs–Helmholtz equation.

The above represents a small selection of properties amenable to thermodynamic analysis. You are invited to review the much more comprehensive undertaking in Section 5.2 and to adapt that scheme to the present situation.

Self Assembly of Monomer Units

We begin here a brief survey of thermodynamic principles for the formation and self-assembly of large-scale aggregates of molecular units, such as polymers, micelles, vesicles, or similar macromolecules. We follow the exposition of Israelachvili.²

As the guiding principle, we use the thermodynamic equilibrium requirement that in a system of identical building blocks, in equilibrium with its aggregates of different sizes, the chemical potential of the various r-mers in different states of assembly be the same. We further ignore the role of solvent in considering the stability of the aggregates relative to the fundamental constituent units. Let $\mu_1, \mu_2, \mu_3, \dots$ be the chemical potentials of the monomers, dimers, trimers, ... relative to their standard values $\mu_1^*, \mu_2^*, \mu_3^*, \dots$ and let x_1, x_2, x_3, \dots be the corresponding mole fractions. Then the equilibrium requirement may be reformulated as follows:

$$\mu \equiv \mu_1^* + RT \ln x_1 = \mu_2^* + \frac{1}{2} RT \ln(x_2) = \mu_3^* + \frac{1}{3} RT \ln(x_3) = \dots \quad (5.4.21)$$

or, more compactly,

$$\mu \equiv \mu_N = \mu_N^* + (RT/N) \ln(x_N/N), \quad (5.4.22a)$$

for the N -mer aggregate. The above may be understood by noting that in a system containing a total of n (in mole numbers) elementary building blocks (*ebbs*), $n_1 = x_1 n$, $n_2 = x_2 n$, $n_3 = x_3 n$, ... *ebbs* are used to assemble $x_1 n$, $x_2 n/2$, $x_3 n/3$, ... monomers, dimers, trimers, ..., respectively. When divided by the volume V of the system, one obtains the concentrations $c_1 = x_1 n/V$, $c_2 = x_2 n/2V$, $c_3 = x_3 n/3V$, ... The Gibbs free energies of the trimers are thus given by $G_3 = G_3^0 + (x_3 n/3) RT \ln(x_3 n/3V)$, where G_3^0 is the Gibbs free energy at unit concentration. Now switch to mole fractions, and absorb the $\ln(n/V)$ factor to define the quantity $G_3^* = G_3^0 + (x_3 n/3) RT \ln(n/V)$ as the Gibbs free energy of $x_3 n/3$ pure trimer units; this jibes with the discussion surrounding Eq. (3.8.13). We therefore set

$$G_3 = G_3^* + n(x_3/3) RT \ln(x_3/3). \quad (5.4.22b)$$

Division by $n x_3$ yields the molar free energy of the trimer as shown in Eq. (5.4.21).

For future reference, note that the term $n(x_3/3) \ln(x_3/3)$ in Eq. (5.4.22b) represents the negentropy of trimers assembled from n *ebbs*. This identification follows from a comparison with Eq. (2.5.10) for the entropy of mixtures; more fundamentally, it is the standard formulation for the entropy of $x_3/3$ units provided by statistical thermodynamics, as shown in Chapter 10. As a result, the remaining term G_3^* in Eq. (5.4.22b) is equivalent to the enthalpy H_3^* for $n/3$ trimers generated from n *ebb* units. On multiplying by three, one obtains the molar enthalpy of trimers $\tilde{H}_3^* = 3\mu_3^*$, a result used later.

In our further deliberations, we set Eq. (5.4.22a), for the N -mer, equal to its counterpart, involving an M -mer in the chain of Eq. (5.4.21). This relation may be solved for

$$\frac{x_N}{N} = \left\{ \left(\frac{x_M}{M} \right) \exp \left[\frac{M(\mu_M^* - \mu_N^*)}{RT} \right] \right\}^{\frac{N}{M}}. \quad (5.4.23a)$$

For the particular case, $M = 1$ this reduces to

$$\frac{x_N}{N} = \left\{ x_1 \exp \left[\frac{\mu_1^* - \mu_N^*}{RT} \right] \right\}^N. \quad (5.4.23b)$$

The above relations, together with the requirement $\sum_N x_N = 1$, define the properties of the system.

We first consider an artificial special case which itself is very instructive. Assume that the interactions between molecules in the aggregated and monodispersed states are the same; then the standard chemical potentials are all equal: $\mu_1^* = \mu_2^* = \mu_3^* = \cdots = \mu_N^*$. In that event, Eq. (5.4.23b) reduces to

$$x_N = Nx_1^N. \quad (5.4.24)$$

Since $x_1 < 1$, it is clear that for large N , $x_N \ll x_1$. In this case, only very small aggregates will be present in the solution, of which the monomer is by far the most stable. This trend is even more accentuated if we now allow the μ_N^* increase with N . Thus, large aggregates cannot be expected to form unless at some stage the μ_N^* start to diminish with rising N and become smaller than μ_1^* . In fact, the variation of μ_N^* with N determines the characteristics of the solution with respect to the state of aggregation of the solute molecules, as we now investigate.

Geometric Effects: Linear Aggregates

The variation of μ^* with N largely depends on geometric considerations. Consider first a set of one-dimensional rod-shaped polymers, and let $\acute{\alpha}_1 RT$ represent the molar bond energy involved in joining two monomers. Assuming that H_N^* is representable by the additivity of bond energies, the earlier discussion leading to the relation $\tilde{H}_N^* = N\mu_N^*$ shows that the standard molar enthalpy of the linear N -mer relative to the nonbonded units is given by

$$N\mu_N^* = -(N-1)\acute{\alpha}_1 RT, \quad (5.4.25)$$

with one fewer bond than the number of *ebbs* in the chain. By a trivial rearrangement, we obtain

$$\mu_N^* = -(1 - 1/N)\acute{\alpha}_1 RT \equiv \mu_\infty^* + \acute{\alpha}_1 RT/N, \quad (5.4.26)$$

Clearly, as the chain length increases, the mean free bonding energy of the rod diminishes toward the “bulk” value μ_∞^* . From the above derivation, it is evident that the last term on the right is proportional to the ratio $2/N$ of the number of terminal atoms to the total number of constituents in the chain.

Two-Dimensional Sheets

For two-dimensional disk structures (Figure 5.4.2), the number of r -mers in a disk is proportional to its area, πR_0^2 , whereas the number of monomer units on the periphery that can bond only to interior molecules is proportional to the circumference, $2\pi R_0$, and hence, proportional to $N^{1/2}$. Thus, the ratio of the two quantities is given by $N^{-1/2}$. In a derivation parallel to that of the one-dimensional case, one is thus led to the result

$$\mu_N^* = \mu_\infty^* + \acute{\alpha}_2 RT/N^{1/2}, \quad (5.4.27)$$

where the multiplier differs in value from the one-dimensional case (see below).

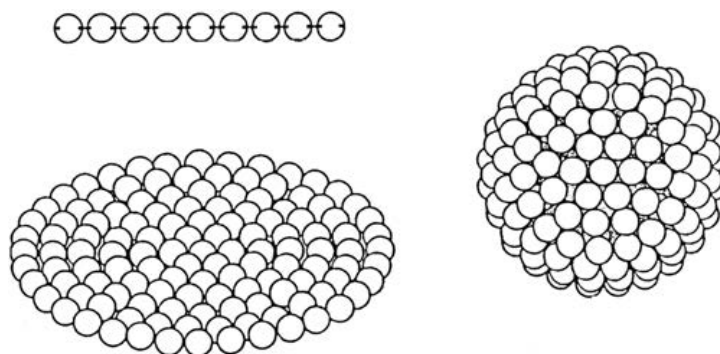


FIGURE 5.4.2

Assembly of dissolved identical monomer units into rods, two-dimensional disks, or three-dimensional spheres.

After Israelachvili, loc. Cit.

Three-Dimensional, Spheroidal Aggregates

In a spherical aggregate, the number of ebb units, r , is proportional to the volume $4\pi R_0^3/3$ of the sphere, whereas the number of monomer units on the spherical surface is proportional to $4\pi R_0^2$, that is, to $N^{2/3}$. The ratio of these two quantities is $N^{-1/3}$, whence, in a derivation analogous to the one-dimensional case, one is led to the result

$$\mu_N^* = \mu_\infty^* + \acute{\alpha}_3 RT/N^{1/3}, \quad (5.4.28)$$

This may be made more evident by considering the case of a small molecule with volume v , whereby in a spherical aggregate, $N = 4\pi R_0^3/3v$. The standard interfacial free energy of the sphere is specified by $N\mu_\infty^* + 4\pi R_0^2\gamma$, where γ is the interfacial free energy per unit area. We therefore write

$$\mu_N^* = \mu_\infty^* + 4\pi R_0^2\gamma/N = \mu_\infty^* + \left(4\pi\gamma/N^{1/3}\right)(3v/4\pi N)^{2/3} = \mu_\infty^* + \acute{\alpha}_3 RT/N^{1/3}, \quad (5.4.29)$$

which shows how $\acute{\alpha}_3$ may be obtained in this particular case.

One should note that for the simple structures enumerated above, the standard free energies are of the general form

$$\mu_N^* = \mu_\infty^* + \acute{\alpha}_N RT/N^q, \quad (5.4.30)$$

where the exponent q depends on the dimensionality of the array. This quantity need not be the reciprocal of an integer; nonintegral values for dimensions are commonplace among fractal aggregates. Note that in all the above cases, with $\acute{\alpha} \equiv \acute{\alpha}_N$ a positive quantity, the standard free energy diminishes with rising N toward its value in an infinite aggregate, as a separate phase. This is a necessary condition for the formation of large-scale structures.

Critical Concentrations

Once μ_N^* is known, as shown above, one can ask: what are the critical concentrations required for formation of aggregates? This may be established by employing Eq. (5.4.30), in which the index is first set at $N = 1$ and then at N , and then inserting these expressions into Eq. (5.4.23b), whereby one obtains

$$x_N = N\{x_1 \exp(\dot{\alpha}(1 - 1/N^q))\}^N \approx N[x_1 e^{\dot{\alpha}}]^N. \quad (5.4.31)$$

For sufficiently low values of x_1 , such that $x_1 e^{\dot{\alpha}} < 1$, $x_N/N < x_1$ for any $N > 1$. For such low-mole fractions, the solution will consist principally of monomer units, with mole fraction x_1 , dissolved in the solvent. However, this inequality no longer applies at higher concentrations: for, by definition, x_N/N for use in Eq. (5.4.31) cannot exceed unity, which means that the quantity in braces is not allowed to exceed unity. In other words, $\exp\{-\dot{\alpha}(1 - 1/N^q)\} = \exp\{-(\mu_1^* - \mu_N^*/RT)\}$ is to be an upper limit on x_1 . This cutoff value represents the critical aggregation mole fraction (CAMF). Thus, when x_N is specified by Eq. (5.4.31), we find that $x_1|_{\text{CAMF}} \approx e^{-\dot{\alpha}}$ for all $q > 1$; at these values of x_1 , any further addition of monomer molecules to the solution results solely in the formation of more aggregates, such that x_1 remains at its upper limit.

Phase Separation vs Finite-Size Aggregates

In addressing this question, we note that for the geometric shapes with $q > 1$ the exact form of Eq. (5.4.31) reads

$$x_N = N[x_1 e^{\dot{\alpha}}]^N e^{-\dot{\alpha}N^{1-q}}. \quad (5.4.32)$$

Clearly, for any positive $\dot{\alpha}$ of reasonable size, the usual case, one does not anticipate the presence of large-scale combinations of monomers. What happens instead is that a separate phase forms, essentially an aggregate of infinite size. It is evident that even for any positive value of $q < 1$ in the above equation, the formation of a separate phase cannot be avoided. Aggregates that fall into this category are those for which the intermolecular bonds are very flexible, so that symmetrically disposed polymeric disk-shaped or bilayer units may be formed. Hence, to develop large aggregates in solution, it is necessary to seek conditions under which, beyond some finite N , the quantity x_N of the system attains a minimum constant value. Such a case will now be considered.

Aggregates for Which $q = 1$; Chain-like and Related Aggregates

We take up the case of systems for which one may set $q = 1$ in Eq. (5.4.32). This leads to the relation,

$$x_N = N[x_1 e^{\dot{\alpha}}]^N e^{-\dot{\alpha}}. \quad (5.4.33)$$

the exponential factor on the right now being a constant. Note that above the CAMF, the quantity $x_1 e^{\dot{\alpha}} \leq 1$, so that initially, for small N , x_N is proportional to N . That is, the aggregates tend to grow in proportion to their size. This trend cannot, however, continue indefinitely; for, ultimately the $N[x_1 e^{\dot{\alpha}}]^N < 1$ factor in Eq. (5.4.33) begins to dominate, thereby diminishing x_N toward zero as N becomes very large. In short, under present circumstances, one anticipates a distribution of aggregate sizes, with a maximum at intermediate values of N . By contrast, Eq. (5.4.32) shows that with $x_1 e^{\dot{\alpha}} \ll 1$

and for $q > 1$, x_N very rapidly plunges toward zero, so that no large-scale aggregates form as dispersed entities in solution. The case $q = 1$ appears to be very specialized; nevertheless, rod-like or chain-like structures, as well as cylindrical micelles, and microfilaments and microtubules fall into this category. Additionally, spherical vesicles and certain classes of microemulsion droplets are members of this class. More generally, it is aggregates for which the intermolecular bonding is very rigid that are members in this category. Thus, it is worthwhile to examine this special case in greater detail.

The total mole fraction of all aggregates dissolved in the solvent is given by

$$x_A = \sum_N x_N = \sum_N N \left[x_1 e^{\dot{\alpha}} \right]^N e^{-\dot{\alpha}} = e^{-\dot{\alpha}} \left[x_1 e^{\dot{\alpha}} + 2 \left(x_1 e^{\dot{\alpha}} \right)^2 + 3 \left(x_1 e^{\dot{\alpha}} \right)^3 + \dots \right] = \frac{x_1}{(1 - x_1 e^{\dot{\alpha}})^2} \quad (5.4.34)$$

where the mathematical identity $\sum_N zN = z/(1 - z)^2$ ($1 \leq N \leq \infty$) had been introduced. We may solve the above quadratic equation for

$$\frac{x_1 = (1 + 2x_A e^{\dot{\alpha}}) - \sqrt{1 + 4x_A e^{\dot{\alpha}}}}{2x_A e^{2\dot{\alpha}}}, \quad (5.4.35)$$

where the minus sign is retained to ensure that x_1 does not exceed unity.

For $x_A e^{\dot{\alpha}} \ll 1$, the expansion of the square root to second-order terms leads to the relation $x_1 = x_A/16$, whereas in the opposite limit, $x_A e^{\dot{\alpha}} \gg 1$,

$$x_1 = \left[1 - \left(x_A e^{\dot{\alpha}} \right)^{-\frac{1}{2}} \right]^N e^{-\dot{\alpha}} \leq e^{-\dot{\alpha}}, \quad (5.4.36)$$

which indicates, as expected, that x_1 approaches the CAMF value.

In the present approximation, the distribution of aggregates of various sizes is found by inserting the above relation into Eq. (5.4.33) to obtain

$$x_N = N \left[1 - \left(x_A e^{\dot{\alpha}} \right)^{-\frac{1}{2}} \right]^N e^{-\dot{\alpha}}. \quad (5.4.37)$$

For large r , this reduces to

$$x_N = N \exp\{-\dot{\alpha}\} \exp\left\{ -N/\sqrt{(x_A e^{\dot{\alpha}})} \right\}, \quad (5.4.38)$$

as may be verified by carrying out a first-order expansion on the second of the above exponential functions and on the multiplier of $N e^{-\dot{\alpha}}$ in Eq. (5.4.37). Equation (5.4.38) has an extremum at $\partial x_N / \partial N = 0$, i.e. at

$$N_{\max} = \sqrt{(x_A e^{\dot{\alpha}})}, \quad (5.4.39)$$

Thus, Eq. (5.4.38) shows that the probability of encountering very large aggregates declines exponentially as $\exp\{-N/N_{\max}\}$.

The expectation value for N is specified by $\langle N \rangle = \sum N x_N / \sum x_N = \sum N x_N / x_A$ (see Eq. (5.4.34)); one finds that

$$\langle N \rangle = \sqrt{(1 + 4x_A e^{\dot{\alpha}})}, \quad (5.4.40a)$$

which reduces to the limits

$$\langle N \rangle = 1 \text{ and } \langle N \rangle = 2\sqrt{x_A e^{\hat{\alpha}}} = 2N_{\max} \quad (5.4.40b)$$

below and above the CAMF, respectively.

A survey of these findings shows that the distribution of aggregation is very broad: it initially rises with N , then peaks, and finally decays to zero for very large N . The distribution is strongly affected by the value of $\hat{\alpha}$.

For much more detailed discussions of this topic, a variety of specialized sources must be consulted.

References

- 5.4.1.** I.N. Levine, *Physical Chemistry* (McGraw Hill, Boston, MA, 2002) 5th Ed., Chap. 13.
5.4.2. J.N. Israelachvily, *Intermolecular and Surface Forces* (Academic Press, London, 1991) 2nd Ed., Chapter 16.
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5.5 Pressure of Electromagnetic Radiation

To prepare for the thermodynamic properties of radiation effects, we consider the pressure exerted by electromagnetic radiation based on Maxwell's equations for electromagnetic fields. The analysis is not as difficult as may appear at first glance. But if you do not wish to wade through the rather lengthy derivation, please note the final result (Eq. (5.5.11)) which is needed for the next section.

Pressure of Electromagnetic Radiation

As shown in Eq. (1.6.5), the force density acting on free charges placed in electromagnetic fields in volume element $d^3\mathbf{r}$ is given by $d\mathbf{f} = (\rho_f \mathcal{E} + c^{-1} \mathbf{J} \times \mathcal{B}) d^3\mathbf{r}$, where ρ_f is the density of free carriers in the system (not to be confused with the electrical resistivity of the material), \mathbf{J} is the corresponding current density, \mathcal{E} is the electric field, \mathcal{B} is the magnetic induction (magnetic flux density vector), and c is the speed of light. The instantaneous pressure exerted on a cross-section $dxdy$ of a wall by incident radiation that penetrates the surface to a thickness $0 \leq z \leq \epsilon$ is given by

$$P_i = df/dxdy = \int_0^\epsilon (\rho_f \mathcal{E} + c^{-1} \mathbf{J} \times \mathcal{B}) dz \equiv \int_0^\epsilon I dz. \quad (5.5.1)$$

The average pressure exerted over one period \mathcal{T} of the incident oscillatory radiation is then found to be

$$P_T = (1/\mathcal{T}) \int_0^T P_i dt = (1/\mathcal{T}) \int_0^T \int_0^\epsilon (\rho_f \mathcal{E} + c^{-1} \mathbf{J} \times \mathcal{B}) dz dt \equiv (1/\mathcal{T}) \int_0^T \int_0^\epsilon I dz dt. \quad (5.5.2)$$

Now use the Maxwell relations $\nabla \cdot \mathcal{E} = 4\pi\rho_f$ and $\nabla \times \mathcal{B} - c^{-1}(\partial\mathcal{E}/\partial t) = 4\pi\mathbf{J}/c$ to eliminate ρ_f and \mathbf{J} from Eq. (5.5.2). We rewrite the integrand \mathbf{I} in the form

$$\mathbf{I} = (4\pi)^{-1}[\nabla \cdot \mathcal{E}]\mathcal{E} + \left[(4\pi)^{-1}\nabla \times \mathcal{E} - (4\pi c)^{-1}(\partial\mathcal{E}/\partial t) \right] \times \mathcal{B}. \quad (5.5.3)$$

The last term on the right is then recast as

$$(\partial\mathcal{E}/\partial t) \times \mathcal{B} = \partial(\mathcal{E} \times \mathcal{B})/\partial t - \mathcal{E} \times (\partial\mathcal{B}/\partial t) = \partial(\mathcal{E} \times \mathcal{B})/\partial t + \mathcal{E} \times [c\nabla \times \mathcal{E}], \quad (5.5.4)$$

where the third Maxwell relation $\nabla \times \mathcal{E} = -c^{-1}(\partial\mathcal{B}/\partial t)$ has been used on the right.

As the next step, insert Eq. (5.5.4) into Eq. (5.5.3):

$$\mathbf{I} = (4\pi)^{-1}[\nabla \cdot \mathcal{E}]\mathcal{E} - (4\pi)^{-1}\mathcal{E} \times [\nabla \times \mathcal{E}] - (4\pi)^{-1}\partial(\mathcal{E} \times \mathcal{B})/\partial t - (4\pi)^{-1}[\mathcal{B} \times (\nabla \times \mathcal{B})]. \quad (5.5.5a)$$

It is expedient to recast the above as

$$\mathcal{J} = \mathcal{E}_\phi - (4\pi c)^{-1}\partial(\mathcal{E} \times \mathcal{B})/\partial t + \mathcal{B}_\phi. \quad (5.5.5b)$$

Next, substitute Eqs. (5.5.5) into Eq. (5.5.2); without loss of generality, we assume the incident radiation to propagate along the z -axis. For monochromatic radiation along z , the electric and magnetic field components \mathcal{E}_k and \mathcal{B}_l vary with time as $\cos(\omega_k t) \times \cos(\omega_l t)$. When the time derivative is taken and the integration over time is performed over one period, the central term in Eq. (5.5.5b) averages to zero. One thus is left with the following expression for the average z -component of the radiation pressure:

$$P|_z = (1/T) \int_0^T \int_0^\epsilon (\mathcal{E}_{\phi z} + \mathcal{B}_{\phi z}) dz dt. \quad (5.5.6)$$

From the definition of \mathcal{E}_ϕ , one obtains by straightforward manipulations

$$\begin{aligned} \mathcal{E}_{\phi z} = & (4\pi)^{-1}\mathcal{E}_z \left[\left(\frac{\partial\mathcal{E}_x}{\partial x} \right) + \left(\frac{\partial\mathcal{E}_y}{\partial y} \right) + \left(\frac{\partial\mathcal{E}_z}{\partial z} \right) \right] - (4\pi)^{-1}\mathcal{E}_x \left[\left(\frac{\partial\mathcal{E}_x}{\partial z} \right) - \left(\frac{\partial\mathcal{E}_z}{\partial x} \right) \right] \\ & + (4\pi)^{-1}\mathcal{E}_y \left[\left(\frac{\partial\mathcal{E}_z}{\partial y} \right) - \left(\frac{\partial\mathcal{E}_y}{\partial z} \right) \right] \end{aligned} \quad (5.5.7a)$$

which may be recast as

$$\mathcal{E}_{\phi z} = (8\pi)^{-1}[\partial(\mathcal{E}_z^2 - \mathcal{E}_x^2 - \mathcal{E}_y^2)/\partial z + (4\pi)^{-1}[\partial(\mathcal{E}_x\mathcal{E}_z)/\partial x + \partial(\mathcal{E}_y\mathcal{E}_z)/\partial y]]. \quad (5.5.7b)$$

An analogous procedure applies to \mathcal{B}_ϕ . Here we also introduce the Maxwell relation $\nabla \cdot \mathcal{B} = 0$ as a trick to expand on the definition for \mathcal{B}_ϕ in Eq. (5.5.5b); namely, we set

$$\mathcal{B}_\phi = (4\pi)^{-1}(\nabla \cdot \mathcal{B})\mathcal{B} - (4\pi)^{-1}\mathcal{B} \times (\nabla \times \mathcal{B}), \quad (5.5.8)$$

which has precisely the same mathematical form as does \mathcal{E}_ϕ , with \mathcal{B} replacing \mathcal{E} . Therefore, we can immediately write

$$\mathcal{B}_{\phi z} = (8\pi)^{-1}[\partial(\mathcal{B}_z^2 - \mathcal{B}_x^2 - \mathcal{B}_y^2)/\partial z + (4\pi)^{-1}[\partial(\mathcal{B}_x\mathcal{B}_z)/\partial x + \partial(\mathcal{B}_y\mathcal{B}_z)/\partial y]]. \quad (5.5.9)$$

The next step involves substitution of Eqs. (5.5.7b) and (5.5.9) into Eq. (5.5.6). We omit all terms such as $\mathcal{B}_y \mathcal{B}_z \sim \mathcal{B}_0^2 \cos(kx - \omega_k t - \phi) \cos(lz - \omega_l t - \phi)$ since integration over one period of the partial derivatives in Eq. (5.5.6) yields a null result. This reduces Eq. (5.5.6) to

$$P|_z = (1/\mathcal{T})(8\pi)^{-1} \int_0^T dt \int_0^\varepsilon dz [\partial(\mathcal{E}_z^2 - \mathcal{E}_x^2 - \mathcal{E}_y^2 + \mathcal{B}_z^2 - \mathcal{B}_x^2 - \mathcal{B}_y^2)/\partial y]. \quad (5.5.10a)$$

In the integration over z we note that, by definition, the electric and magnetic field vectors vanish at $z = \varepsilon$, so that the integrand is zero at the upper limit of the integral. The vectors have their maximum impact values—hence their values in free space—at the surface of the wall, $z = 0$. Therefore, Eq. (5.5.10a) assumes the form

$$P|_z = (1/\mathcal{T})(8\pi)^{-1} \int_0^T dt (-\mathcal{E}_z^2 + \mathcal{E}_x^2 + \mathcal{E}_y^2 - \mathcal{B}_z^2 + \mathcal{B}_x^2 + \mathcal{B}_y^2). \quad (5.5.10b)$$

In the time integration over one period, we replace a term such as $(1/\mathcal{T}) \times \int_0^T dt \mathcal{E}_z^2$ by its average, $\langle \mathcal{E}_z^2 \rangle$, and we subsequently set $\langle \mathcal{E}^2 \rangle = \langle \mathcal{E}_x^2 \rangle + \langle \mathcal{E}_y^2 \rangle + \langle \mathcal{E}_z^2 \rangle$, and similarly for $\langle \mathcal{B}_z^2 \rangle$. This leads to the result

$$P|_z = (8\pi)^{-1} [\langle \mathcal{E}^2 \rangle - 2\langle \mathcal{E}_z^2 \rangle + \langle \mathcal{B}^2 \rangle - 2\langle \mathcal{B}_z^2 \rangle]. \quad (5.5.10c)$$

At equilibrium, we assume that the radiation is completely isotropic. With no distinction in direction the average values, all the components of \mathcal{E}^2 are the same, so that $\langle \mathcal{E}_x^2 \rangle = \langle \mathcal{E}_y^2 \rangle = \langle \mathcal{E}_z^2 \rangle = \langle \mathcal{E}^2 \rangle/3$, and similarly for the components of $\langle \mathcal{B}^2 \rangle$. This leads to the final expression

$$P|_z = (1/3) \left[(8\pi)^{-1} (\langle \mathcal{E}^2 \rangle + \langle \mathcal{B}^2 \rangle) \right] \equiv u/3. \quad (5.5.11)$$

As is well established, and as will be demonstrated by noncircular arguments in later sections, the quantity in square brackets in the above equation represents the energy density of an electromagnetic field in vacuo, designated here as u . This establishes the expression on the right. The result $P|_z = (u/3)$ will be used below. Very crudely, one may argue that the transport of isotropic energy density u along one direction should be one-third of the total.

5.6 Thermodynamic Characterization of Electrodynamic Radiation

Here we discuss the description of electromagnetic radiation in equilibrium with the walls of an evacuated cavity that contains a tiny porthole for experimental observations. This addresses the point raised by scientists in the mid-1800s, who insisted that one needed to understand the properties of heat and of radiation to explain the fundamental processes we encounter in the universe. The former have been discussed at length; we now deal with the latter.

If the walls are opaque and form an ideal black body, the nature of the radiation is independent of the quality of the walls and depends solely on the temperature. To prove this assertion, consider two cavities, made of different materials, which are connected through a tube that permits radiation to be passed back and forth. Let the cavities be initially at the same temperature and assume that by virtue of its superior composition cavity, B is capable of “attracting” more radiation than cavity A. Then the

uneven flow of radiation would cause the walls of chamber B to receive additional energy and to heat up. In short, heat would flow spontaneously from a cooler to a warmer body, in contravention to the corollary to the second law. Thus, the radiation intensity can depend only on the temperature T of the walls; for, it is an experimental fact that as T is raised the nature of the radiation inside the cavity is observed to change. We first examine the thermodynamic characterization of the radiation in equilibrium with the black body, and then turn to quantum and statistical mechanics for a full description.

Pressure of Impinging Radiation

Electromagnetic radiation impinging on a wall exerts a pressure P_c that will be determined via a classical argument. Referring to Figure 5.6.1, consider radiation contained in a cylinder of length cdt and cross-section dA whose long axis is at an angle θ with respect to the axis perpendicular to the wall. In the time dt , all electromagnetic radiation traveling with velocity c will emerge from the cylinder to hit the slab. The corresponding incident momentum is given by $dA p c dt$, where \mathbf{p} is the momentum density vector of the radiation. If that radiation is totally absorbed by the surface, then the corresponding force exerted on the plate is found from Newton's Law as the time rate of change of momentum, involving the speed c :

$$d\mathbf{F}(\theta, \phi) = dA \mathbf{p}(\theta, \phi) c, \quad (5.6.1)$$

where ϕ is the azimuthal angle about the perpendicular axis, taken to coincide with the z direction. As long as the radiation is isotropic, one obtains the above contribution at every angle θ and ϕ . In integrating first over ϕ , the \mathbf{F} components parallel to the surface sum to zero, and only those along the z -axis, perpendicular to the wall, are additive. The perpendicular component is thus given by

$$dF_{\perp}(\theta) = dA p(\theta, \phi) c \cos \theta. \quad (5.6.2)$$

The cross-sectional area on the surface, dA_{\perp} , being larger than that of the cylinder, is specified as $dA_{\perp} = dA \cos \theta$. Thus, the pressure exerted by the radiation may be written as

$$P_r(\theta) = dF_{\perp} / dA_{\perp} = p(\theta) c \cos^2 \theta, \quad (5.6.3)$$

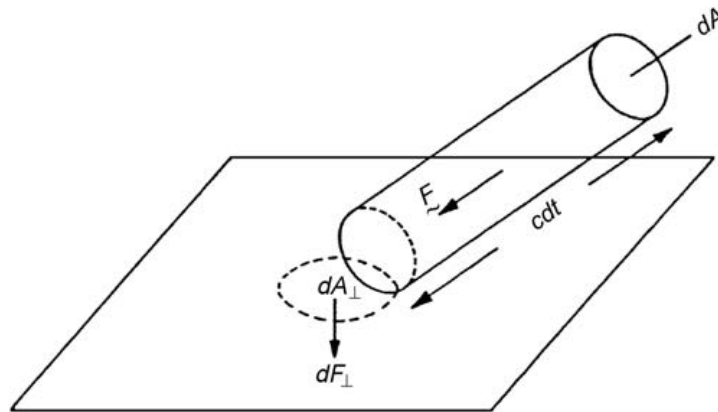


FIGURE 5.6.1

Figure illustrating the radiation inside a cylinder of a cross-section dA and length cdt impinging on a wall in time dt and exerting a force dF_{\perp} perpendicular to the plane.

which is to be attributed to all radiation incident on the slab at an angle θ . When averaging over all angles, we obtain

$$\bar{P}_r \int_0^{\pi/2} 2\pi \sin \theta d\theta = pc \int_0^{\pi/2} 2\pi \cos^2 \theta \sin \theta d\theta. \quad (5.6.4)$$

On evaluating the integrals, one obtains

$$\bar{P}_r = (1/3)pc = (1/3)u. \quad (5.6.5)$$

On the right, we have introduced Einstein's formulation for the relation between energy density u and momentum density p of electromagnetic radiation, namely $pc = u$. A classical derivation of the above expression was furnished in the preceding section.

Thermodynamics of Electrodynamic Radiation

For the thermodynamic analysis, we begin with the standard expression

$$TdS = dU + \bar{P}_r dV, \quad (5.6.6a)$$

which may be rewritten as

$$T(\partial S/\partial V)_T = (\partial U/\partial V)_T + \bar{P}_r. \quad (5.6.6b)$$

On invoking the appropriate Maxwell relation, we find

$$T(\partial \bar{P}_r/\partial T)_V = (\partial U/\partial V)_T + \bar{P}_r. \quad (5.6.6c)$$

Recall that at fixed T , $u = u(T)$ is constant and $\bar{P}_r = u/3$. Moreover, $U \equiv uV$; then

$$(1/3)T(du/dT) = (\partial uV/\partial V)_T + (1/3)u = (4/3)u, \quad (5.6.7)$$

which simplifies to

$$T(du/dT) = 4u. \quad (5.6.8)$$

The solution of this differential equation is given by $\ln u = 4\ln T + \ln \sigma$, where σ is an arbitrary constant. This may be rewritten in the form

$$u = \sigma T^4. \quad (5.6.9)$$

The above relation is known as the *Stefan–Boltzmann Law* (1879); the constant is empirically determined to be $\sigma = 5.67 \times 10^{-8} \text{ W/K}^4\text{m}^2$. One should note the very strong dependence of the energy density of the electromagnetic radiation on the temperature.

We obtain the entropy for electromagnetic radiation from the expression

$$ds = (dU + \bar{P}_r dV)/T. \quad (5.6.10)$$

On setting $uV = U = \sigma T^4 V$ and $\bar{P}_r = u/3$, we obtain

$$dS = [Vdu + (\bar{P}_r + u)dV]/T, \quad (5.6.11a)$$

so that in view of Eq. (5.6.9),

$$dS = (4\sigma/3)(3VT^2dT + T^3dV), \quad (5.6.11b)$$

which, at fixed temperature T , becomes ($\partial S/\partial V \equiv s$), and

$$s = (4/3)\sigma T^3; \quad S = (4/3)\sigma T^3V, \quad (5.6.12)$$

which is the desired relation.

Other functions of state are obtained by writing

$$A = U - TS = -(1/3)\sigma T^4V \quad (5.6.13)$$

and

$$G = A + \bar{P}_rV = 0. \quad (5.6.14)$$

Notice that the Gibbs free energy of electromagnetic radiation vanishes identically. This apparently peculiar result correlates with the fact that electromagnetic radiation consists of energy packets—quanta. These discrete units, called *photons*, are elementary particles subject to Bose Einstein statistics, as discussed in Chapter 10. Their densities depend on the intensity of the radiation according to the Planck distribution law, proportional to $[\exp(h\nu/k_BT) - 1]^{-1}$. Here h represents the Planck's constant, ν is the frequency of the radiation, and k_B is the Boltzmann's constant. The quanta, $h\nu$, are not real particles since their density can be changed through temperature adjustments. Since n_{ph} depends on T , it is not an independent variable, so that one cannot allow terms of the type $\mu_{\text{ph}}dn_{\text{ph}}$ to appear in the expression for dG . To guarantee consistency in the theory, one must therefore require that μ_{ph} vanish; $G = 0$ as applied to electromagnetic radiation.

Determination of the Stefan–Boltzmann Constant

To determine the value of σ in Eq. (5.6.9), we first consider electromagnetic radiation inside a rectangular enclosure of edge length L in equilibrium with the black walls at temperature T . Classically, this situation is characterized by positing that the radiation inside the cavity consists of standing waves with discrete wavelengths λ that can be accommodated (properly “fit”) within the range $[0, L]$ along each of the three orthogonal directions. This can only be the case if the fit along, say, the x direction for the wave number $k_x = 2\pi/\lambda$ exactly matches $k_x = n_x\pi/L$, so that $n_x\lambda/2 = L$; an integral number n_x of half wavelengths properly stretches along x from one side of the enclosure to the other.

The rest of the analysis hinges on the solution to the wave equation governing the propagation of electromagnetic waves, given by

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\mathcal{E}(\mathbf{r}, t) = \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathcal{E}(\mathbf{r}, t), \quad (5.6.15)$$

where $\mathcal{E}(\mathbf{r}, t)$ represents the electric field vector in its dependence on position \mathbf{r} and time t and c represents the velocity of light. Casual inspection verifies that the solution to the wave equation is given by

$$\mathcal{E}_x = \mathcal{E}_{0x} \sin(\omega t) \cos(k_x x) \sin(k_y y) \sin(k_z z) \quad (5.6.16a)$$

$$\mathcal{E}_y = \mathcal{E}_{0y} \sin(\omega t) \sin(k_x x) \cos(k_y y) \sin(k_z z) \quad (5.6.16b)$$

$$\mathcal{E}_z = \mathcal{E}_{0z} \sin(\omega t) \sin(k_x x) \sin(k_y y) \cos(k_z z) \quad (5.6.16c)$$

provided the following condition is met, namely

$$k_x^2 + k_y^2 + k_z^2 = \omega^2/c^2. \quad (5.6.17)$$

In view of the fitting condition, this translates as

$$\left(\frac{n_x \pi}{L}\right)^2 + \left(\frac{n_y \pi}{L}\right)^2 + \left(\frac{n_z \pi}{L}\right)^2 = \frac{\omega^2}{c^2}, \quad n\lambda \text{ an integer} \quad (5.6.18)$$

or ($k = c/\omega$)

$$n_x^2 + n_y^2 + n_z^2 = \frac{L^2 \omega^2}{\pi^2 c^2} = \frac{V^{2/3}}{\pi^2} k^2; \quad (n_x^2 + n_y^2 + n_z^2)^{1/2} = \frac{V^{1/3}}{\pi} k(\omega). \quad (5.6.19)$$

The right-hand side may be represented in terms of a quantum space spanned by n_x , n_y , and n_z , in which the integers are represented as discrete points, surrounded by an exclusion volume $(\pi/L)^3$. $(n_x^2 + n_y^2 + n_z^2)^{1/2}$ then is equivalent to a radius vector for a sphere of radius $V^{1/3}k(\omega)/\pi$ that contains all possible integers meeting the requirement of Eq. (5.6.19). However, their enumeration must be confined to one octant, to eliminate redundancies in counting the number of unique integers that satisfy Eq. (5.6.19). The number of such lattice points is given by

$$\mathcal{N} = \frac{1}{8} \frac{4\pi}{3} \left[\frac{V^{1/3}k(\omega)}{\pi} \right]^3, \quad (5.6.20)$$

and the density of states is found by differentiation:

$$\mathcal{D}(\omega)d\omega = \frac{V}{2\pi^2} k^2(\omega) \frac{\partial k(\omega)}{\partial \omega} d\omega. \quad (5.6.21)$$

This finally allows us to set up an expression for the Helmholtz free energy. On the assumption that the spacing between successive quantized states is sufficiently small to allow the use of continuum variables, we introduce the partition function appropriate to Bose statistics (Chapter 10) and set $\beta \equiv 1/k_B T$, so that

$$A = k_B T \int_0^\infty \ln(1 - e^{-\beta \hbar \omega}) \mathcal{D}(\omega) d\omega. \quad (5.6.22)$$

Next, we introduce a factor of two to account for the two transverse modes of propagation of radiation, set $k = c/\omega$, and introduce Eq. (5.6.21), whence

$$A = \frac{V k_B T}{\pi^2 c^3} \int_0^\infty \omega^2 \ln(1 - e^{-\beta \hbar \omega}) d\omega. \quad (5.6.23)$$

The energy is then specified by $U = A - TS = A - T\partial A/\partial T = \partial(\beta A)/\partial\beta$, so that

$$U = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \omega^3 d\omega = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty \frac{1}{e^{\beta\hbar\omega} - 1} \omega^3 d\omega. \quad (5.6.24)$$

The integral on the right is of the form $(\hbar\beta)^{-4} \int_0^\infty (e^z - 1)^{-1} z^3 dz$ for which the integral is known to converge to $\pi^2/15$. Accordingly,

$$U = \frac{\pi^2 k_B^4}{15\hbar^3 c^3} VT^4 \equiv bT^4, \quad (5.6.25)$$

in agreement with Eq. (5.6.9).

To study the equilibrated radiation, we drill a tiny observation hole into the cavity and observe the emerging beam. Its radiation energy density U/V emerges in all forward directions with speed c . What is observed is the component of the beam along the direction of sight, namely $u \cos \theta$ (where $\theta = 0$ along the line of sight), while the perpendicular components over all azimuthal angles $0 \leq \phi \leq 2\pi$ sum to zero. The integration over $0 \leq \theta \leq \pi/2$ is given by $u \int_0^{\pi/2} \cos \theta \sin \theta d\theta = u/2$. Similarly, the photons emerge with velocity c over all forward directions; again only the components along the line of sight count; this yields a second factor, $c/2$. Hence, the energy-density flux is given by

$$J_u = \frac{cU}{4V} = \frac{c}{4} \left(\frac{\pi^2 k_B^4}{15\hbar^3 c^3} \right) T^4 \equiv \sigma_B T^4, \quad (5.6.26)$$

We have thus determined the relevant multiplier of T^4 from fundamental principles.

Exercises

- 5.6.1.** Derive an expression for the heat capacity of electromagnetic radiation and determine its value for unit volume at 1 K, 300 K, and 30,000 K. Compare these values with those of a monatomic ideal gas at room temperature. At what temperature do these quantities become equal?
- 5.6.2.** In the early history of the cosmos temperatures of 10^6 K were common. What was the radiation pressure at that time?
- 5.6.3.** Contrast the relation $P_r = u/3$ with a comparable expression for a monatomic gas.

5.7 Effects of Electric Fields on Thermodynamic Properties of Matter

Now, onto a study of the thermodynamic properties of matter exposed to electromagnetic fields! We ease into this subject by way of a preliminary discussion. The material will be repeated and expanded upon in the next section; for a more complete and yet more systematic exposition, please examine a review article.¹ Obviously, you may proceed directly to the more orderly presentation in Section 5.8.

Recall the relevant element of work establishing an electric field and then placing a material with polarization vector \mathcal{P} into the field. The expression for the work is exhibited in Eq. (1.6.8) and Section 1.7; in the absence of magnetic fields,

$$dW = (4\pi)^{-1} \int d^3\mathbf{r} \mathbf{E}_0 \cdot d\mathbf{E}_0 - \int_V d^3\mathbf{r} \mathcal{P} \cdot d\mathbf{E}_0. \quad (5.7.1)$$

Here \mathbf{E}_0 is the applied electric field prior to insertion of the sample. The system is assumed to be totally surrounded by empty space. In that event, \mathbf{E}_0 is the applied electric field in free space arising from a distribution of generating charges placed in confines beyond that space. The disposition and magnitude of these charges is changeable and so designed that the electric field remains unaltered when a test system is immersed in the electric field. Since $\mathcal{P} = 0$ in the vacuum outside the sample, the second integration may be limited to the confines V of the system, whereas the first integral must be taken over the entire space over which \mathbf{E}_0 extends. However, this term involves the work of generating the electric field in vacuum, and therefore, usually is of no immediate interest. So, we frequently drop this term. Next, we introduce the constitutive relation $\mathcal{P} = \alpha_0 \mathbf{E}_0$ that specifies the polarization dependence of an isotropic material on the applied electric field. Tensorial notation is required in case the response of the material is anisotropic, as is shown in Sections 5.10 and 5.11. Also, higher order terms in \mathbf{E}_0 may be needed if nonlinear responses arise in sufficiently strong applied fields. The quantity α_0 is termed the *polarizability* of the material, a quantity that is measured experimentally, and that depends on the density and temperature of the system.

Isothermal Responses

We begin with the first law of thermodynamics. We drop the vectorial notation for materials that are isotropic in their response to the electric field. Including the energy required to establish the electric field in vacuo, the differential form of the total energy of the system of constant composition may be written as

$$dU = TdS - PdV + (4\pi)^{-1} \int d^3\mathbf{r} \mathbf{E}_0 \cdot d\mathbf{E}_0 - \int_V d^3\mathbf{r} \mathcal{P} \cdot d\mathbf{E}_0. \quad (5.7.2)$$

Next, for convenience, we switch directly to the differential form of the Helmholtz free energy, $A = U - TS$:

$$dA = -SdT - PdV + (4\pi)^{-1} \int d^3\mathbf{r} \mathbf{E}_0 \cdot d\mathbf{E}_0 - \int_V d^3\mathbf{r} \mathcal{P} \cdot d\mathbf{E}_0. \quad (5.7.3)$$

Clearly, A is here considered to be a function of T , V , and \mathbf{E}_0 .

Now let V and T remain fixed, and assume isotropy, which allows us to dispense with vectorial notation. Then,

$$dA|_{T,V} = (4\pi)^{-1} \int d^3\mathbf{r} \mathbf{E}_0 \cdot d\mathbf{E}_0 - \int_V d^3\mathbf{r} \mathcal{P} \cdot d\mathbf{E}_0|_{T,V}. \quad (5.7.4)$$

We next introduce the Helmholtz free-energy density a through the relation $A = \int_V d^3\mathbf{r} a$; comparison with Eq. (5.7.4) establishes that

$$da|_{T,V} = (4\pi)^{-1} \mathbf{E}_0 \cdot d\mathbf{E}_0 - \mathcal{P} \cdot d\mathbf{E}_0|_{T,V}. \quad (5.7.5)$$

Now apply the constitutive relation to a material of steady composition $\mathcal{P} = \alpha_0(T, V)\epsilon_0$, and assume that the polarizability does not depend on the electric field. Phenomena such as ferroelectricity and hysteresis are thereby excluded from consideration. Such materials are said to be “linear”. As usual, we also assume reversible operations. Then Eq. (5.7.5) may be readily integrated with respect to \mathcal{E}_0 ; we obtain

$$a(T, V, \mathcal{E}_0) - a(T, V, 0) = \mathcal{E}_0^2/8\pi - \alpha_0(T, V)\mathcal{E}_0^2/2 = \mathcal{E}_0^2/8\pi - \alpha_0(T, V)\mathcal{E} \cdot \mathcal{P}/2. \quad (5.7.6)$$

As is obvious, it is the second term in the middle or on the right that exhibits the response of the matter to the field, in terms of its Helmholtz free-energy density.

The entropy density is found from the relation

$$s = -(\partial a/\partial T)_{V, \mathcal{E}_0}, \quad (5.7.7)$$

which, on differentiation of Eq. (5.7.6) with respect to T , leads to

$$s(T, V, \mathcal{E}_0) - s(T, V, 0) = (\mathcal{E}_0^2/2)(\partial \alpha_0/\partial T)_V = (\mathcal{E}_0/2) \cdot (\partial \mathcal{P}/\partial T)_V. \quad (5.7.8)$$

Here one should note that $(\partial \alpha_0/\partial T)_V$ and $(\partial \mathcal{P}/\partial T)_V$ for all materials are negative: the (at least) partial alignment of the elementary dipoles of the system by the electric field is increasingly counteracted by a rise in temperature that tends to destroy the degree of order. Note further that in vacuo both α_0 and \mathcal{P} vanish; as is reasonable, empty space permeated by a steady electric field does not carry any entropy.

The energy density is obtained from the relation $e = a + Ts$:

$$\begin{aligned} e(T, V, \mathcal{E}_0) - e(T, V, 0) &= \mathcal{E}_0^2/8\pi - (\mathcal{E}_0^2/2)[\alpha_0 - T(\partial \alpha_0/\partial T)_V] \\ &= \mathcal{E}_0^2/8\pi - (\mathcal{E}_0 \cdot \mathcal{P}/2)[1 - T(\partial \ln \alpha_0/\partial T)_V]. \end{aligned} \quad (5.7.9)$$

Equation (5.7.6) is sometimes labeled as the energy density of the system in an electric field, but in light of Eq. (5.7.9), this is clearly an erroneous statement.

The radiation pressure exerted by the field may be determined from the relation $P_r = -(\partial A/\partial V)_T$. The partial differentiation process called for here is not straightforward because the volume, which is one of the independent variables, occurs as an integration limit in Eq. (5.7.4). For the present, we circumvent this difficulty by assuming that \mathcal{P} (not to be confused with P) is homogeneous throughout the sample, so that it varies solely with the temperature and may then be taken outside the integral, thereby bypassing the problem. This cannot be strictly correct because, minimally, surface regions differ in their polarization from the bulk; in fact, in electrodynamic theory, surface regions are treated as separate entities. A more sophisticated treatment to address this matter is developed later. For now, we rewrite Eq. (5.7.6) in the form

$$A(T, V, \mathcal{E}_0) - A(T, V, 0) = \mathcal{E}_0^2/8\pi - V\alpha_0(T, V)\mathcal{E}_0^2/2. \quad (5.7.10)$$

The radiation pressure is obtained by differentiation as

$$P_r = P(0) + \alpha_0(T, V)\mathcal{E}_0^2/2 + V(\mathcal{E}_0^2/2)(\partial \alpha_0/\partial V)_T, \quad (5.7.11)$$

where the first term on the right represents the pressure in the absence of the field. One should note the quadratic dependence of P_r and A on \mathcal{E}_0 . This tallies with the conclusions reached in Sec. 5.5, where it was shown that $P_r \sim u \sim \mathcal{E}_0^2$.

Adiabatic Response

We have so far considered isothermal conditions. To handle the adiabatic response, we consider S , V , and \mathcal{E}_0 to be the fundamental variables that relate to the energy U , whose differential form is specified in Eq. (5.7.2). Under reversible isochoric and adiabatic conditions for a material of constant composition, and with $dU = \int d\mathbf{r}^3 du|_{S,V}$, we find that

$$du|_{S,V} = (4\pi)^{-1} \mathcal{E}_0 \cdot d\mathcal{E}_0 - \mathcal{P} \cdot d\mathcal{E}_0|_{S,V} = (4\pi)^{-1} \mathcal{E}_0 \cdot d\mathcal{E}_0 - \alpha_0(T, V) \mathcal{E}_0 \cdot d\mathcal{E}_0|_{S,V}. \quad (5.7.12)$$

Note that on integrating over the field at constant entropy, the temperature of the system necessarily changes, so that in contrast to the earlier treatment, $\alpha_0(T, V)$ now varies during integration. In fact, since $S = S(T, V, \mathcal{E}_0)$, we must first invert this relation to specify $T = T(S, V, \mathcal{E}_0)$, so that the polarizability is written out as $\alpha_0(S(T, V, \mathcal{E}_0), V) = \alpha_0(S, V, \mathcal{E}_0)$. We then integrate Eq. (5.7.12) by parts to find

$$u(S, V, \mathcal{E}_0) - u(S, V, 0) = \frac{\mathcal{E}_0^2}{8\pi} - \frac{\alpha_0(S, V, \mathcal{E}_0) \mathcal{E}_0^2}{2} + \int_V \left(\frac{\mathcal{E}_0^2}{2} \right) \left(\frac{\partial \alpha_0}{\partial \mathcal{E}_0} \right)_{S,V} d\mathcal{E}_0. \quad (5.7.13)$$

The entropy differential is given by

$$dS = (\partial S / \partial T)_{V, \mathcal{E}_0} dT + (\partial S / \partial V)_{T, \mathcal{E}_0} dV + (\partial S / \partial \mathcal{E}_0)_{V, T} d\mathcal{E}_0. \quad (5.7.14)$$

We now specialize to isochoric, isentropic (i.e. adiabatic) conditions, $dV = dS = 0$ and we replace the first partial derivative with c_e/T , where c_e , in place of C_V , is the corresponding heat capacity. Use lower case letters to denote the densities and set $c_e = \int_V c_e d^3\mathbf{r}$. Then the above reduces to

$$(c_e/T) dT|_{S,V} = -(\partial s / \partial \mathcal{E}_0)_{V, T} d\mathcal{E}_0|_{S,V} = -\mathcal{E}_0 (\partial \alpha_0 / \partial T)_{S,V} \cdot d\mathcal{E}_0|_{S,V}, \quad (5.7.15)$$

where Eq. (5.7.8) has been applied. The integration can be carried out after the dependence of c_e and of α_0 on T has been inserted. This procedure furnishes the interrelation between the temperature and electric field under adiabatic conditions, $T = T(V, \mathcal{E}_0)$.

Equation (5.7.15) is actually deceptively simple; for, at constant S the temperature changes with the application of the electric field. Thus, one must rewrite $\alpha_0(S(T, V), V, \mathcal{E}_0)$ so as to involve temperature as the variable and then introduce the quantity $T = T(V, \mathcal{E}_0)$ wherever T occurs in $\alpha_0(T, V)$ before proceeding. It is therefore easier to introduce this step in Eq. (5.7.12) prior to carrying out the integration.

Electric Field Effects at Constant Temperature and Pressure

When T and P are held fixed, it is appropriate to return to the Gibbs free-energy function analogous to Eq. (5.7.3),

$$dG = -SdT + VdP + (4\pi)^{-1} \int d^3\mathbf{r} \mathcal{E}_0 \cdot d\mathcal{E}_0 - \int_V d^3\mathbf{r} \mathcal{P} \cdot d\mathcal{E}_0. \quad (5.7.16)$$

Assume constant P and T , and define $dG_e \equiv dG - (4\pi)^{-1} \int d^3\mathbf{r} \mathcal{E}_0 \cdot d\mathcal{E}_0$, so that the new differential relates solely to the materials properties. Then, introduce the Gibbs free-energy density $g(\mathbf{r}, T, P, \mathcal{E}_0)$, so as to write the differential form as

$$dG_e|_{T,P} = \left[\left(\frac{\partial}{\partial \mathcal{E}_0} \right) \int_{V(T,P,\mathcal{E}_0)} d^3\mathbf{r} g(\mathbf{r}, T, P, \mathcal{E}_0) \right]_{T,P} d\mathcal{E}_0 = - \int_{V(T,P,\mathcal{E}_0)} d^3\mathbf{r} \mathcal{P} \cdot d\mathcal{E}_0|_{T,P}. \quad (5.7.17)$$

One must proceed with caution because V in the limits of the integral is no longer constant. However, for the present, let us assume that the integrands in the middle and on the right are independent of \mathbf{r} . Equation (5.7.17) may then be replaced by

$$\left[\frac{\partial(V(T, P, \mathbf{E}_0)g(T, P, \mathbf{E}_0))}{\partial \mathbf{E}_0} \right]_{T,P} d\mathbf{E}_0 = -V(T, P, \mathbf{E}_0)\alpha_0(T, V(T, P, \mathbf{E}_0))\mathbf{E}_0 \cdot d\mathbf{E}_0|_{T,P}, \quad (5.7.18)$$

so that on integration, we obtain formally

$$\begin{aligned} V(T, P, \mathbf{E}_0)g(T, P, \mathbf{E}_0) - V(T, P, 0)g(T, P, 0) &= G(T, P, \mathbf{E}_0) - G(T, P, 0) \\ &= - \int V(T, P, \mathbf{E}_0)\alpha_0(T, V(T, P, \mathbf{E}_0))\mathbf{E}_0 \cdot d\mathbf{E}_0|_{T,P}. \end{aligned} \quad (5.7.19)$$

The integration over \mathbf{E}_0 on the right requires that we specify the variation of volume with applied electric field. In the event that we are allowed to ignore this dependence, we find for linear materials for which α_0 is independent of \mathbf{E}_0 ,

$$g(T, P, \mathbf{E}_0) - g(T, P, 0) = -\alpha_0(T, V(T, P))/\mathbf{E}_0^2/2, \quad (5.7.20)$$

which, in the present approximation, coincides with Eq. (5.7.6). However, if we wish to continue using Eq. (5.7.19) without further approximation, we must determine how V and α_0 change with \mathbf{E}_0 . This is accomplished by using Maxwell equations, as shown below.

Use of Maxwell's Relations

Here we illustrate how Maxwell's equations may be utilized. From Eq. (5.7.16), we obtain

$$\partial^2 G_e / \partial \mathbf{E}_0 \partial T = -(\partial S / \partial \mathbf{E}_0)_{T,P} = \partial^2 G_e / \partial T \partial \mathbf{E}_0 = -(\partial / \partial T) \left[\int_{V(T,P,\mathbf{E}_0)} d^3 \mathbf{r} \mathcal{P} \right]_{T,P}. \quad (5.7.21)$$

We replace S by the entropy density s so as to write

$$(\partial S / \partial \mathbf{E}_0)_{T,P} = (\partial / \partial \mathbf{E}_0) \left[\int_{V(T,P,\mathbf{E}_0)} d^3 \mathbf{r} s(\mathbf{r}, T, V, \mathbf{E}_0) \right]_{T,P}. \quad (5.7.22)$$

The differentiations called for in the last two equations again involve integrals with variable limits. For simplicity, we once more assume that the integrands s and P are uniform throughout the sample; then on equating Eqs. (5.7.21) and (5.7.22), we set

$$[\partial(Vs) / \partial \mathbf{E}_0]_{T,P} = [\partial(V\mathcal{P}) / \partial T]_{P,\mathbf{E}_0}, \quad (5.7.23)$$

which, in the approximations introduced so far, may be integrated to yield (for linear materials)

$$S(T, P, \mathbf{E}_0) - S(T, P, 0) = \left[\alpha_0(T, V(T, P)) \left(\frac{\partial V}{\partial T} \right)_P + V(T, P) \left(\frac{\partial \alpha_0}{\partial T} \right)_P \right] \mathbf{E}_0^2/2. \quad (5.7.24)$$

With the above simplification, a second relation of interest is derived from Eq. (5.7.17) by the cross-differentiation

$$(\partial^2 G_e / \partial \mathcal{E}_0 \partial P) = (\partial V / \partial \mathcal{E}_0)_{T,P} = (\partial^2 G_e / \partial P \partial \mathcal{E}_0) = - \left[\frac{\partial(V(T, P, \mathcal{E}_0) \mathcal{P}(T, P, \mathcal{E}_0))}{\partial P} \right]_{T, \mathcal{E}_0}. \quad (5.7.25)$$

Integration of the simplified expression leads to

$$V(T, P, \mathcal{E}_0) - V(T, P, 0) = - \int V(T, P, \mathcal{E}_0) \left(\frac{\partial \alpha_0}{\partial P} \right)_{T, \mathcal{E}_0} \mathcal{E}_0 \cdot d\mathcal{E}_0 - \int \left[\alpha_0(T, V(T, P, \mathcal{E}_0)) \right] \left(\frac{\partial V}{\partial P} \right)_{T, \mathcal{E}_0} \mathcal{E}_0 \cdot d\mathcal{E}_0. \quad (5.7.26)$$

Actually, Eq. (5.7.26) is an integro-differential equation since the unknown V appears on the left-hand side as well as under the integral sign; techniques for solving such an equation are available in standard mathematical treatises. In the present case, however, an iterative method should work well because the changes of V with \mathcal{E}_0 are likely to be small.

A more systematic approach to the entire subject will be presented next.

Reference and Exercises

- 5.7.1.** J.M. Honig and L.L. Van Zandt, *J. Franklin Inst.* **323**, 297 (1987).
- 5.7.2.** Derive expressions showing how the heat capacity of a material at constant pressure and constant volume changes with application of an electric field.
- 5.7.3.** Establish Maxwell relations based on Eqs. (5.7.2) and (5.7.3) and discuss their utility.
- 5.7.4.** Compare the two expressions for entropy density variations with an applied electric field and discuss the implications of your findings.

5.8 Systematization of Electromagnetic Field Effects in Thermodynamics

Let us now generalize and systematize the discussion of the previous section by including the thermodynamic properties of magnetic fields, and by proceeding in a more orderly fashion. The starting point, as usual, is the first law; it now contains the elements of work associated with both electric and magnetic fields. We derived the fundamental expression for the element of work in Section 1.6. At the outset, let us discard the terms $\mathcal{E}_0^2/8\pi$ and $\mathcal{H}_0^2/8\pi$ for electromagnetic field effects in free space. The remaining contributions involve the integral shown below that was derived for the differential of the energy, namely,

$$dU' = TdS - PdV + \int_V d^3\mathbf{r} (-\mathcal{P} \cdot d\mathcal{E}_0 + \mathcal{H}_0 \cdot d\mathcal{M}). \quad (5.8.1)$$

Note that this particular formulation involves the magnetization density \mathcal{M} as the relevant independent magnetic variable. The above equation is perfectly appropriate; unfortunately, the magnetization is not

subject to direct experimental control. Experimentalists would greatly prefer a version in which \mathcal{H}_0 —the applied magnetic field prior to insertion of the sample—occurs as the relevant independent variable; this particular quantity can be controlled at will. To achieve the desired end, we introduce the following Legendre transformation:

$$dU \equiv dU' - d\left(\int_V d^3\mathbf{r} \mathcal{M} \cdot \mathcal{H}_0/V\right). \quad (5.8.2)$$

Here, we encounter the persistent problem of having to deal with differentials or derivatives of integrals with variable limits. Procedures for handling this problem were detailed in Section 1.3. On applying this method, using Eq. (1.3.36), we rewrite the above as

$$dU = dU' - \int_V d^3\mathbf{r} (\mathcal{M} \cdot d\mathcal{H}_0 + \mathcal{H}_0 \cdot d\mathcal{M}) - \left[\int_V d^3\mathbf{r} (\mathcal{M} \cdot \mathcal{H}_0/V) \right] dV. \quad (5.8.3)$$

In the last term, the integral is a multiplier of dV and therefore represents a contribution to the measured pressure generated by the magnetic field. We thus introduce the symbol

$$P_m \equiv P + \int_V d^3\mathbf{r} (\mathcal{M} \cdot \mathcal{H}_0/V) \quad (5.8.4)$$

for the generalized pressure appropriate to the present formulation. The differential of the energy involving the independent variables S , V , \mathcal{E}_0 , and \mathcal{H}_0 therefore takes the form

$$dU = TdS - P_m dV - \int_V d^3\mathbf{r} (\mathcal{P} \cdot d\mathcal{E}_0 + \mathcal{M} \cdot d\mathcal{H}_0). \quad (5.8.5a)$$

Application of the standard Legendre transformations that preserve \mathcal{E}_0 and \mathcal{H}_0 as independent variables yields the remaining functions of state:

$$dH = TdS + VdP_m - \int_V d^3\mathbf{r} (\mathcal{P} \cdot d\mathcal{E}_0 + \mathcal{M} \cdot d\mathcal{H}_0) \quad (5.8.5b)$$

$$dA = -SdT - P_m dV - \int_V d^3\mathbf{r} (\mathcal{P} \cdot d\mathcal{E}_0 + \mathcal{M} \cdot d\mathcal{H}_0) \quad (5.8.5c)$$

$$dG = -SdT + VdP_m - \int_V d^3\mathbf{r} (\mathcal{P} \cdot d\mathcal{E}_0 + \mathcal{M} \cdot d\mathcal{H}_0). \quad (5.8.5d)$$

The above equations represent differential forms properly adapted to describe electromagnetic phenomena in terms of applied fields. It has not always been properly recognized that the use of $\mathcal{M} \cdot d\mathcal{H}_0$ as a magnetic work element also entails the replacement of mechanical pressure P by Eq. (5.8.4).

We continue to employ volume integrals in dealing with electromagnetic phenomena because in the standard theory, the polarization and magnetization generally vary throughout the sample; in

particular, effects in the bulk differ from those of the surface. Thus, \mathcal{P} and \mathcal{M} are intrinsically non-uniform even when they may be absolutely constant in the bulk of the sample.

In what follows we introduce constitutive relations, assuming that \mathcal{P} and \mathcal{M} are collinear with \mathcal{E}_0 and \mathcal{H}_0 , respectively. In that case, we dispense with vectorial notation to write

$$\mathcal{P} = \alpha_0 \mathcal{E}_0 \quad \text{and} \quad \mathcal{M} = \chi_0 \mathcal{H}_0. \quad (5.8.6)$$

Here, $\alpha_0(T, V)$ and $\chi_0(T, V)$ represent, respectively, the modified scalar *electric polarizability* and *magnetic susceptibility*.¹ As before, we assume that these parameters do not depend on the intensity of the applied electromagnetic field; such materials are said to be “linear” in their response to electromagnetic fields. Phenomena such as ferroelectricity and ferromagnetism are thus excluded from the current formulations, as are effects achieved in high intensity fields, for which higher powers in \mathcal{E}_0 and \mathcal{H}_0 are needed.

Clearly, whenever \mathcal{H}_0 occurs as an independent variable, all original thermodynamic functions that involved the pressure P must now be changed to the generalized pressure P_m . In particular, under equilibrium conditions where $dG = 0$, it is not just the mechanical pressure, but the magnetic component as well that must be uniform throughout the sample. This point is not sufficiently emphasized in many discussions.

In examining the fundamental relations (Eqs. (5.8.5)), note that we can define another 12 functions of state, in which the functions corresponding to U , H , A , and G are specified in terms of $(\mathcal{P}, \mathcal{H}_0)$, or $(\mathcal{E}_0, \mathcal{M})$, or $(\mathcal{P}, \mathcal{M})$ as the independent electromagnetic variables. None of these sets is less fundamental than are the functions (Eqs. (5.8.5)). We adopt Eqs. (5.8.5) because, as already emphasized, \mathcal{E}_0 and \mathcal{H}_0 are subject to direct experimental control. Henceforth we drop the vector notation altogether.

First-Order Partial Derivatives

We begin a systematic exploration of the thermodynamic functions by partial differentiation of Eqs. (5.8.5) as follows:

$$S = -(\partial A / \partial T)_{V, \mathcal{E}_0, \mathcal{H}_0} = -(\partial G / \partial T)_{P_m, \mathcal{E}_0, \mathcal{H}_0} \quad (5.8.7a)$$

$$P_m = -(\partial A / \partial V)_{T, \mathcal{E}_0, \mathcal{H}_0} = -(\partial U / \partial V)_{S, \mathcal{E}_0, \mathcal{H}_0} \quad (5.8.7b)$$

$$V = (\partial G / \partial P_m)_{T, \mathcal{E}_0, \mathcal{H}_0} = (\partial H / \partial P_m)_{S, \mathcal{E}_0, \mathcal{H}_0} \quad (5.8.7c)$$

$$T = (\partial U / \partial S)_{V, \mathcal{E}_0, \mathcal{H}_0} = (\partial H / \partial S)_{P_m, \mathcal{E}_0, \mathcal{H}_0} \quad (5.8.7d)$$

$$\bar{P} = -(\partial A / \partial \mathcal{E}_0)_{T, V, \mathcal{H}_0} = -(\partial G / \partial \mathcal{E}_0)_{T, P_m, \mathcal{H}_0} = -(\partial U / \partial \mathcal{E}_0)_{S, V, \mathcal{H}_0} = -(\partial H / \partial \mathcal{E}_0)_{S, P_m, \mathcal{H}_0} \quad (5.8.7e)$$

$$\bar{M} = -(\partial A / \partial \mathcal{H}_0)_{T, V, \mathcal{E}_0} = -(\partial G / \partial \mathcal{H}_0)_{T, P_m, \mathcal{E}_0} = -(\partial U / \partial \mathcal{H}_0)_{S, V, \mathcal{E}_0} = -(\partial H / \partial \mathcal{H}_0)_{S, P_m, \mathcal{E}_0}. \quad (5.8.7f)$$

Here, we defined $\bar{P} \equiv \int_V d^3 \mathbf{r} \mathcal{P}$ and $\bar{M} \equiv \int_V d^3 \mathbf{r} \mathcal{M}$. Equations (5.8.7a–5.8.7d) are straightforward extensions of the results cited in Section 1.12. The remaining equations indicate how the electric and magnetic polarizations change in applied electric or magnetic fields. In taking derivatives, the integrals \bar{P} and \bar{M} are handled in a manner analogous to the treatment of the remaining coefficients T , S , V , and P_m , but care must be taken when dealing with differentials involving volumes. The expressions for

\bar{P} and \bar{M} are especially useful if the Helmholtz or Gibbs free energies are known (e.g. from theoretical considerations) in their dependence on these fields.

Maxwell Relations

Equations (5.8.5) may be used to obtain 24 Maxwell relations by cross-differentiation; these are listed in Table 5.8.I. Several of these arise as trivial modifications of those specified in Section 1.12. The new expressions involve partial derivatives of either $\int_V d^3\mathbf{r}\mathcal{P}$ or $\int_V d^3\mathbf{r}\mathcal{M}$ with respect to independent variables. The order of differentiation and integration may not be interchanged unless the volume is kept fixed. If V is variable, the machinery of Section 1.3 and/or an adaptation of Eq. (1.3.6) must be employed to evaluate the pertinent derivatives; some examples are provided below. A number of interrelations are useful for starting further derivations; they show, for example, how P_m varies with \mathcal{E}_0 or \mathcal{H}_0 under a variety of fixed conditions (lines h, l, t, and x), or how the entropy depends on electromagnetic fields (lines a, e, g, and k). Still others pertain to an interrelation between electric or magnetic polarizations in applied fields under various constraints (lines c, i, o, and u). Other interrelations specify either electrostrictive or magnetostrictive effects (lines b, f, n, and r). We shall later reexamine some of these phenomena.

Table 5.8.I Maxwell Relations Based on the (\mathcal{E}_0, H_0) set of the Thermodynamic Functions

From Eq. (5.8.5d)	From Eq. (5.8.5b)
(a) $(\partial S/\partial E_0)_{T, P_m, H_0} = (\partial \bar{P}/\partial T)_{P_m, E_0, H_0}$	(m) $(\partial T/\partial E_0)_{S, P_m, H_0} = -(\partial \bar{P}/\partial S)_{P_m, E_0, H_0}$
(b) $(\partial V/\partial E_0)_{T, P_m, H_0} = -(\partial \bar{P}/\partial P_m)_{T, E_0, H_0}$	(n) $(\partial V/\partial E_0)_{S, P_m, H_0} = -(\partial \bar{P}/\partial P_m)_{S, E_0, H_0}$
(c) $(\partial \bar{P}/\partial H_0)_{T, P_m, E_0} = (\partial \bar{M}/\partial E_0)_{T, P_m, H_0}$	(o) $(\partial \bar{P}/\partial H_0)_{S, P_m, E_0} = (\partial \bar{M}/\partial E_0)_{S, P_m, H_0}$
(d) $(\partial S/\partial P_m)_{T, E_0, H_0} = -(\partial V/\partial T)_{P_m, E_0, H_0}$	(p) $(\partial T/\partial P_m)_{S, E_0, H_0} = (\partial V/\partial S)_{P_m, E_0, H_0}$
(e) $(\partial S/\partial H_0)_{T, P_m, E_0} = (\partial \bar{M}/\partial T)_{P_m, E_0, H_0}$	(q) $(\partial T/\partial H_0)_{S, P_m, E_0} = -(\partial \bar{M}/\partial S)_{P_m, E_0, H_0}$
(f) $(\partial V/\partial H_0)_{T, P_m, E_0} = -(\partial \bar{M}/\partial P_m)_{T, E_0, H_0}$	(r) $(\partial V/\partial H_0)_{S, P_m, E_0} = -(\partial \bar{M}/\partial P_m)_{S, E_0, H_0}$
From Eq. (5.8.5c)	From Eq. (5.8.5a)
(g) $(\partial S/\partial E_0)_{T, V, H_0} = (\partial \bar{P}/\partial T)_{V, E_0, H_0}$	(s) $(\partial T/\partial E_0)_{S, V, H_0} = -(\partial \bar{P}/\partial S)_{V, E_0, H_0}$
(h) $(\partial P_m/\partial E_0)_{T, V, H_0} = (\partial \bar{P}/\partial V)_{T, E_0, H_0}$	(t) $(\partial P_m/\partial E_0)_{S, V, H_0} = (\partial \bar{P}/\partial V)_{S, E_0, H_0}$
(i) $(\partial \bar{P}/\partial H_0)_{T, V, E_0} = (\partial \bar{M}/\partial E_0)_{T, V, H_0}$	(u) $(\partial \bar{P}/\partial H_0)_{S, V, E_0} = (\partial \bar{M}/\partial E_0)_{S, V, H_0}$
(j) $(\partial S/\partial V)_{T, E_0, H_0} = (\partial P_m/\partial T)_{V, E_0, H_0}$	(v) $(\partial T/\partial V)_{S, E_0, H_0} = -(\partial P_m/\partial S)_{V, E_0, H_0}$
(k) $(\partial S/\partial H_0)_{T, V, E_0} = (\partial \bar{M}/\partial T)_{V, E_0, H_0}$	(w) $(\partial T/\partial H_0)_{S, V, E_0} = -(\partial \bar{M}/\partial S)_{V, E_0, H_0}$
(l) $(\partial P_m/\partial H_0)_{T, V, E_0} = (\partial \bar{M}/\partial V)_{T, E_0, H_0}$	(x) $(\partial P_m/\partial H_0)_{S, V, E_0} = (\partial \bar{M}/\partial V)_{S, E_0, H_0}$
Note $\bar{P} \equiv \int_V d^3\mathbf{r}\mathcal{P}$, $\bar{M} \equiv \int_V d^3\mathbf{r}\mathcal{M}$, $P_m \equiv P + \int_V d^3\mathbf{r}\mathcal{M}\mathcal{H}_0/V$. Underlined quantities represent fixed electromagnetic variables. \mathcal{E}_0 and H_0 are applied electric and magnetic fields prior to insertion of sample.	

You can obviously readily construct three other sets of 24 Maxwell relations, for a grand total of 96, that are based on the differential forms for the various thermodynamic functions involving $(\mathcal{P}, \mathcal{H}_0)$ or $(\mathcal{E}_0, \mathcal{M})$ or $(\mathcal{P}, \mathcal{M})$ as the electromagnetic variables. These determinations are happily left as exercises.

Thermodynamic Equations of State

Further useful information is obtained from Eq. (5.8.5a) in strict analogy to the method used in Section 1.12. We consider the entropy to be a function of T , V , \mathcal{E}_0 , and \mathcal{H}_0 ; accordingly, on using the unnatural coordinates for a closed system to write $U = U(T, V, \mathcal{E}_0, \mathcal{H}_0)$, we set

$$\begin{aligned} dU &= (\partial U / \partial T)_{V, \mathcal{E}_0, \mathcal{H}_0} dT + (\partial U / \partial V)_{T, \mathcal{E}_0, \mathcal{H}_0} dV + (\partial U / \partial \mathcal{E}_0)_{T, V, \mathcal{H}_0} d\mathcal{E}_0 + (\partial U / \partial \mathcal{H}_0)_{T, V, \mathcal{E}_0} d\mathcal{H}_0 \\ &= T(\partial S / \partial T)_{V, \mathcal{E}_0, \mathcal{H}_0} dT + \left[T(\partial S / \partial V)_{T, \mathcal{E}_0, \mathcal{H}_0} - P_m \right] dV + \left[T(\partial S / \partial \mathcal{E}_0)_{T, V, \mathcal{H}_0} - \int_V d^3 \mathbf{r} \mathcal{P} \cdot \right] d\mathcal{E}_0 \\ &\quad + \left[T(\partial S / \partial \mathcal{H}_0)_{T, V, \mathcal{E}_0} - \int_V d^3 \mathbf{r} \mathcal{M} \cdot \right] d\mathcal{H}_0. \end{aligned} \quad (5.8.8)$$

On matching coefficients and introducing Maxwell relations j, g, k from Table 5.8.I, we find that

$$(\partial U / \partial T)_{V, \mathcal{E}_0, \mathcal{H}_0} = T(\partial S / \partial T)_{V, \mathcal{E}_0, \mathcal{H}_0} \equiv C_{V, \mathcal{E}_0, \mathcal{H}_0} \quad (5.8.9a)$$

$$(\partial U / \partial V)_{T, \mathcal{E}_0, \mathcal{H}_0} = T(\partial P_m / \partial T)_{V, \mathcal{E}_0, \mathcal{H}_0} - P_m \quad (5.8.9b)$$

$$(\partial U / \partial \mathcal{E}_0)_{T, V, \mathcal{H}_0} = T(\partial \bar{P} / \partial T)_{V, \mathcal{E}_0, \mathcal{H}_0} - \int_V d^3 \mathbf{r} \mathcal{P} \quad (5.8.9c)$$

$$(\partial U / \partial \mathcal{H}_0)_{T, V, \mathcal{E}_0} = T(\partial \bar{M} / \partial T)_{V, \mathcal{E}_0, \mathcal{H}_0} - \int_V d^3 \mathbf{r} \mathcal{M}. \quad (5.8.9d)$$

Precisely similar methods are applied to determine the thermodynamic equations of state for the enthalpy. Thus,

$$(\partial H / \partial T)_{P_m, \mathcal{E}_0, \mathcal{H}_0} = T(\partial S / \partial T)_{P_m, \mathcal{E}_0, \mathcal{H}_0} \equiv C_{P_m, \mathcal{E}_0, \mathcal{H}_0} \quad (5.8.10a)$$

$$(\partial H / \partial P_m)_{T, \mathcal{E}_0, \mathcal{H}_0} = -T(\partial V / \partial T)_{P_m, \mathcal{E}_0, \mathcal{H}_0} + V \quad (5.8.10b)$$

$$(\partial H / \partial \mathcal{E}_0)_{T, P_m, \mathcal{H}_0} = T(\partial \bar{P} / \partial T)_{P_m, \mathcal{E}_0, \mathcal{H}_0} - \int_V d^3 \mathbf{r} \mathcal{P} \quad (5.8.10c)$$

$$(\partial H / \partial \mathcal{H}_0)_{T, P_m, \mathcal{E}_0} = T(\partial \bar{M} / \partial T)_{P_m, \mathcal{E}_0, \mathcal{H}_0} - \int_V d^3 \mathbf{r} \mathcal{M}. \quad (5.8.10d)$$

In principle, the above partial differential equations may be integrated to find how U and H change with their respective variables of integration. Equations (5.8.9a), (5.8.9b), (5.8.10a) and (5.8.10b) are handled as described in Section 1.12. The remaining relations must be approached carefully. Assuming

linearity of response and constant composition, we write $\alpha_0 = \alpha_0(T, V)$, as well as $\chi_0 = \chi_0(T, V)$, thereby neglecting their electromagnetic field dependence. We also adopt Eq. (5.8.6). Since the $(\partial/\partial T)$ operation in Eqs. (5.8.9c) and (5.8.9d) is to be carried out at fixed V , there is no problem in the interchange of $(\partial/\partial T)$ with $\int_V d^3\mathbf{r}$. Also, the subsequent integration over \mathcal{E}_0 may be carried out independently of the integration over space. From Eq. (5.8.9c), we therefore obtain

$$U(T, V, \mathcal{E}_0) - U(T, V, 0) = (\mathcal{E}_0^2/2) \int_V d^3\mathbf{r} \{T(\partial\alpha_0/\partial T)_V - \alpha_0(T, V)\}, \quad (5.8.11a)$$

and correspondingly,

$$U(T, V, \mathcal{H}_0) - U(T, V, 0) = (\mathcal{H}_0^2/2) \int_V d^3\mathbf{r} \{T(\partial\chi_0/\partial T)_V - \chi_0(T, V)\}. \quad (5.8.11b)$$

Equation (5.8.11a) duplicates Eq. (5.7.9); Eq. (5.8.11b) is its obvious magnetic analog.

To provide an explicit example, we now introduce *Curie's law* for the temperature dependence (described as condition κ) $\alpha_0 = A_e/T, \chi_0 = A_h/T$; this ignores the small diamagnetic correction to the susceptibility, which quantity is independent of the temperature. This relation is derived in Section 10.8. We also set $(\partial V/\partial T)_{P_m, \mathcal{E}_0, \mathcal{H}_0} \approx (\partial V/\partial T)_P = \alpha V$. Here, α (with dimensions of reciprocal temperature, set here in Roman lettering) represents the isobaric expansion coefficient, not to be confused with α_0 (in italics); A_e and A_h are the parameters that are deemed independent of volume; we further ignore any temperature variation of α . Where these conditions obtain, the above relations simplify to

$$U - U_0 = -A_e V \mathcal{E}_0^2/T; \text{ and } U - U_0 = -A_h V \mathcal{H}_0^2/T. \quad (5.8.11c)$$

Note the dependence of U on temperature and field variables for this particular case. One of the reasons why the energy of the system is lowered in an electromagnetic field was mentioned earlier and is repeated below. The alignment of electric and magnetic dipoles of the material becomes more ordered, whence the entropy is diminished.

The corresponding procedure involving Eqs. (5.8.10c) and (5.8.10d) is more complicated because now P_m rather than V is to be held fixed; moreover, α_0 and χ_0 depend on V rather than on P_m directly. One must therefore invoke Eq. (1.3.6) and the procedure associated with Eq. (1.3.35) to deal with the mathematical niceties; these are perfectly straightforward though somewhat messy in detail.³ We find that

$$H(T, P_m, \mathcal{E}_0) - H(T, P_m, 0) = (\mathcal{E}_0^2/2) \left[TI - \int_V d^3\mathbf{r} \alpha_0(T, V) \right], \quad (5.8.12a)$$

in which

$$\begin{aligned} I(T, P_m, \mathcal{E}_0, \mathcal{H}_0) \equiv & \int_V d^3\mathbf{r} \left[\left(\frac{\partial \alpha_0(T, V)}{\partial T} \right)_{V, \mathcal{E}_0, \mathcal{H}_0} + \left(\frac{\partial V(T, P_m, \mathcal{E}_0, \mathcal{H}_0)}{\partial T} \right)_{P_m, \mathcal{E}_0, \mathcal{H}_0} \right. \\ & \left. \times \left\{ \frac{\alpha_0(T, V(T, P_m, \mathcal{E}_0, \mathcal{H}_0))}{V(T, P_m, \mathcal{E}_0, \mathcal{H}_0)} + \left(\frac{\partial \alpha_0(T, V)}{\partial V} \right)_{T, \mathcal{E}_0, \mathcal{H}_0} \right\} \right]. \end{aligned} \quad (5.8.12b)$$

This is clearly more complicated than having to deal with the function U . Do recognize that while H involves P_m as an independent variable, the volume V is a dependent variable. An analogous relation holds for the dependence of H on \mathcal{H}_0 ; this requires the replacement of \mathcal{E}_0 and α_0 , respectively, by \mathcal{H}_0 and χ_0 . The above equation is greatly simplified by introducing Curie's Law κ , which also eliminates the dependence of α_0 on volume; we obtain

$$H(T, V(T, P_m, \mathcal{E}_0, \mathcal{H}_0), \mathcal{E}_0) - H(T, V(T, P_m, 0, 0), 0) = (VA_e/T)(\mathcal{E}_0^2/2)[\alpha T - 2] \quad (5.8.12c)$$

$$H(T, V(T, P_m, \mathcal{E}_0, \mathcal{H}_0), \mathcal{H}_0) - H(T, V(T, P_m, 0, 0), 0) = (VA_h/T)(\mathcal{H}_0^2/2)[\alpha T - 2], \quad (5.8.12d)$$

which should be compared with Eq. (5.8.11c); again, here α is the isobaric expansion coefficient. Note also the dependence of the thermodynamic functions on the square of the electrodynamic fields.

Electromagnetic Effects for Isothermal—Isochoric Conditions

Variations of several thermodynamic functions with electromagnetic fields under conditions of constant T and V are readily handled. Equation (5.8.5c) is rewritten through the string of relations in the form indicated below; no problems arise in the interchange between integration and differentiation:

$$\begin{aligned} dA|_{T,V,\mathcal{H}_0} &= d \int_V d^3r a|_{T,V,\mathcal{H}_0} = \int_V d^3r da|_{T,V,\mathcal{H}_0} = - \int_V d^3r \mathcal{P} \cdot d\mathcal{E}_0|_{T,V,\mathcal{H}_0} \\ &= - \int_V d^3r \alpha_0(T, V) \mathcal{E}_0 \cdot d\mathcal{E}_0|_{T,V,\mathcal{H}_0}, \end{aligned} \quad (5.8.13)$$

which specifies the differential of the Helmholtz free-energy density as $a|_{T,V,\mathcal{H}_0} = -\alpha_0(T, V) \mathcal{E}_0 \cdot d\mathcal{E}_0|_{T,V,\mathcal{H}_0}$, whose integration (with $\mathcal{H}_0 = 0$) yields

$$a(T, V, \mathcal{E}_0) - a(T, V, 0) = -\alpha_0(T, V) \mathcal{E}_0^2/2. \quad (5.8.14a)$$

In precisely the same manner, it may be shown that

$$a(T, V, \mathcal{H}_0) - a(T, V, 0) = -\chi_0(T, V) \mathcal{H}_0^2/2. \quad (5.8.14b)$$

On adoption of Curie's Law κ , we obtain

$$a(T, V, \mathcal{E}_0) - a(T, V, 0) = -A_e \mathcal{E}_0^2/2T; \quad a(T, V, \mathcal{H}_0) - a(T, V, 0) = -A_h \mathcal{H}_0^2/2T. \quad (5.8.14c)$$

We next determine the entropy density via

$$S = \int_V d^3r s = -(\partial A/\partial T)_{V,\mathcal{E}_0,\mathcal{H}_0} = - \left[(\partial/\partial T) \int_V d^3r da \right]_{V,\mathcal{E}_0,\mathcal{H}_0} = - \int_V d^3r (\partial a/\partial T)_{V,\mathcal{E}_0,\mathcal{H}_0}, \quad (5.8.15a)$$

or

$$s = -(\partial a/\partial T)_{V,\mathcal{E}_0,\mathcal{H}_0}. \quad (5.8.15b)$$

Using Eq. (5.8.14a), one readily finds

$$s(T, V, \mathcal{E}_0) - s(T, V, 0) = (\mathcal{E}_0^2/2)(\partial\alpha_0/\partial T)_V. \quad (5.8.16a)$$

In the same manner,

$$s(T, V, \mathcal{H}_0) - s(T, V, 0) = \left(\frac{\mathcal{H}_0^2}{2}\right) \left(\frac{\partial\chi_0}{\partial T}\right)_V. \quad (5.8.16b)$$

Again adopting condition κ , the above expressions reduce to

$$s - s_0 = -A_e \mathcal{E}_0^2/2T^2; \quad s - s_0 = -A_h \mathcal{H}_0^2/2T^2; \quad (5.8.16c)$$

This approximation should be compared with the energy densities Eq. (5.8.11c). It has already been mentioned that the entropy of materials is lower in an electromagnetic field than in the absence of such a field.

Another quantity of interest based on Eq. (5.8.7b) is the generalized pressure; here one must be careful about the variable limit of integration. With the methodology of Section 1.12, we obtain

$$P_m = -(\partial A/\partial V)_{T, \mathcal{E}_0, \mathcal{H}_0} = -\left[(\partial/\partial V) \int_V d^3\mathbf{r} a\right]_{T, \mathcal{E}_0, \mathcal{H}_0} = -\int_V d^3\mathbf{r} \left[a/V + (\partial a/\partial V)_{T, \mathcal{E}_0, \mathcal{H}_0}\right]. \quad (5.8.17a)$$

Substitution from Eq. (5.8.14b) then yields the expression of interest. For an explicit relation, assume that χ_0 is independent of position within the material; one then finds

$$P_m = P + \{\chi_0(T, V) + V(\partial\chi_0/\partial V)_T\} \mathcal{H}_0^2/2. \quad (5.8.17b)$$

If we adopt condition κ , the partial derivative drops out and

$$P_m = P + A_h \mathcal{H}_0^2/2T. \quad (5.8.17c)$$

This expression shows the magnitude of the magnetic contribution to the mechanical pressure; at elevated magnetic fields, this contribution may not be negligible and may even become dominant.

In Eqs. (5.8.11), (5.8.12) and (5.8.14), we specified U , H and A in terms of T , P_m or V , \mathcal{E}_0 , and \mathcal{H}_0 . The determination of G is more involved: we base our derivation on the Gibbs–Helmholtz equation (Eq. (1.12.16)) adapted to the present situation. This is actually an ordinary differential equation of standard form since all variables save T are fixed. Invoking Eq. (1.3.27) as the solution to the first-order differential equation, Eq. (1.12.16), one obtains the expression,⁴

$$G(T, P_m, \mathcal{E}_0) - G(T, P_m, 0) = -T(\mathcal{E}_0^2/2) \left[\int (1/T^2) \left\{ TI - \int_V d^3\mathbf{r} \alpha_0(T, V) \right\} dT \right], \quad (5.8.18a)$$

which looks deceptively simple; however, I is specified by Eq. (5.8.12b), so that the required integration over T is not necessarily trivial. But if again condition κ is adopted, the above simplifies to

$$G(T, P_m, \mathcal{E}_0) - G(T, P_m, 0) = -(\mathcal{E}_0^2 V A_e/2)(1/T - \alpha). \quad (5.8.18b)$$

An analogous expression applies to the magnetic field dependence. These expressions should be compared with Eq. (5.8.14c); throughout, the limitations imposed by the assumptions inherent in condition κ should be clearly kept in mind.

Adiabatic Conditions

In Section 5.7, the adiabatic response of a system to an electric field was discussed in detail. We handle magnetic field effects in the customary manner by rewriting Eq. (5.7.15), using Eq. (5.8.16b):

$$(c_m/T)dT|_{S,V} = -(\partial s/\partial \mathcal{H}_0)_{V,T}d\mathcal{H}_0|_{S,V} = -\mathcal{H}_0 \cdot (\partial \chi_0/\partial T)_{S,V}d\mathcal{H}_0|_{S,V}. \quad (5.8.19)$$

For further progress, we revert to Eq. (5.8.1), set $\mathcal{E}_0 = 0$ and determine

$$(\partial U'/\partial \mathcal{H}_0)_{T,V} = T(\partial S/\partial \mathcal{H}_0)_{T,V} + \int_V d^3r \mathcal{H}_0 \cdot (\partial \mathcal{M}/\partial \mathcal{H}_0)_{T,V}. \quad (5.8.20)$$

Next, introduce the Maxwell relation, line k of Table 5.8.I, as well as the energy density $\int_V d^3r u' \equiv U'$. We then obtain

$$(\partial u'/\partial \mathcal{H}_0)_{T,V} = T(\partial \mathcal{M}/\partial T)_{V,\mathcal{H}_0} + \mathcal{H}_0 \cdot (\partial \mathcal{M}/\partial \mathcal{H}_0)_{T,V}. \quad (5.8.21)$$

This expression is of intrinsic interest: for many classes of materials, the magnetic moment is known to be an entire function of \mathcal{H}_0/T , in which case, as is readily verified, $(\partial u'/\partial \mathcal{H}_0)_{T,V} = 0$. Then u' and U' do not depend on \mathcal{H}_0 , in which case the heat capacity is a function of T and of V alone.

Now use the defining relation $U = U' - \int_V d^3r \mathcal{H}_0 \cdot \mathcal{M}$, and differentiate with respect to T at constant V and \mathcal{H}_0 to obtain

$$c_{V,\mathcal{H}_0} = c'_{V,\mathcal{H}_0} - \mathcal{H}_0 \cdot (\partial \mathcal{M}/\partial T)_{V,\mathcal{H}_0}. \quad (5.8.22)$$

For a large class of materials, it is found empirically that $c'_{V,\mathcal{H}_0} = A_1/T^2$, and that $\mathcal{M} = A_2\mathcal{H}_0/T$ is an entire function of \mathcal{H}_0/T ; here A_1 and A_2 are independent of \mathcal{H}_0 and T . On introducing these results in Eq. (5.8.22), we obtain

$$c_{V,\mathcal{H}_0} = A_1/T^2 + A_2(\mathcal{H}_0/T)^2. \quad (5.8.23)$$

This example shows how the heat capacity varies with temperature and magnetic field in this particular instance. This relation provides another avenue for finding the energy of a system subjected to magnetization, by integration of Eq. (5.8.23) with respect to T .

Comments and Assignments

5.8.1. We use the term modified electric polarizability and modified magnetic susceptibility because in the standard literature, these quantities relate \mathcal{P} to \mathcal{E} , rather than to \mathcal{E}_0 , and \mathcal{M} to \mathcal{P} , rather than to \mathcal{H}_0 .

- 5.8.2.** Set up 12 additional functions of state whose independent variables involve $(\mathcal{P}, \mathcal{M})$, $(\mathcal{P}, \mathcal{H}_0)$, and $(\mathcal{M}, \mathcal{E}_0)$. Discuss their utility. Derive Maxwell relations based on these state functions and identify those that you deem useful.
- 5.8.3.** We define $I = \left(\partial \left\{ \int_V d^3 \mathbf{r} \alpha_0(T, V) \right\} / \partial T \right)$. By Eqs. (1.3.34) and (1.3.35), the differentiation yields $I = \int_V d^3 \mathbf{r} \left(\frac{\partial \alpha_0}{\partial T} \right)_{P_m, \mathcal{E}_0, \mathcal{H}_0} + \int_V d^3 \mathbf{r} \frac{\alpha_0}{V} \left(\frac{\partial V}{\partial T} \right)_{P_m, \mathcal{E}_0, \mathcal{H}_0}$. Using Eq. (1.3.6), the first integral may be rewritten as $\int_V d^3 \mathbf{r} \left[\left(\frac{\partial \alpha_0}{\partial T} \right)_{V, \mathcal{E}_0, \mathcal{H}_0} + \left(\frac{\partial \alpha_0}{\partial V} \right)_{T, \mathcal{H}_0, \mathcal{E}_0} \left(\frac{\partial V}{\partial T} \right)_{P_m, \mathcal{E}_0, \mathcal{H}_0} \right]$. On insertion in the above, we recover Eq. (5.8.12b).
- 5.8.4.** The solution of the first-order differential equation has the form $G(T, P_m, \mathcal{E}_0, \mathcal{H}_0) = e^{\ln T} \left\{ dT e^{-\ln T} \left(-\frac{\mathcal{H}(T, P_m, \mathcal{E}_0, \mathcal{H}_0)}{T} \right) \right\} + C$, where C is a constant, that is evaluated by setting $\mathcal{E}_0 = 0$. Then $G(T, P_m, \mathcal{E}_0, \mathcal{H}_0) - G(T, P_m, 0, \mathcal{H}_0) = -T \left\{ \int dT \left(\frac{\mathcal{H}(T, P_m, \mathcal{E}_0, \mathcal{H}_0) - \mathcal{H}(T, P_m, 0, \mathcal{H}_0)}{T^2} \right) \right\}$, into which we substitute from Eqs. (5.8.12).
- 5.8.5.** Derive relations for the physical properties of materials whose magnetization follows the *Curie–Weiss* law: $\mathcal{M} = A_2 \mathcal{H}_0 / (T + \Theta)$, where Θ is a parameter, called the *Weiss constant*.
- 5.8.6.** Check on the expression (5.8.14) by basing your derivation on the Gibbs–Helmholtz relation and solving the first-order differential equation.
- 5.8.7.** Show that when Curie’s law holds, (a) U and CM are the functions of T alone; (b) $S = S_0 + V^2 \mathcal{M}^2 / 2C'$; (c) $c_{\mathcal{H}_0} - C_{\mathcal{M}} = V^2 \mathcal{M}^2 / 2C'$; also (d) $(\partial C_{\mathcal{H}_0} / \partial \mathcal{H}_0)_T = 2C' \mathcal{H}_0 / T^2$. Here C' is the Curie constant.
- 5.8.8.** Show that $(\partial U / \partial \mathcal{H}_0)_{V, T} = T[(\partial(V\mathcal{M}) / \partial T)_{V, \mathcal{H}_0} + (\partial(V\mathcal{M})_{\mathcal{H}_0} / \partial \mathcal{H}_0)_{V, T}]$. Derive an analogous relation for $(\partial H / \partial \mathcal{H}_0)_{P_m, T}$.
- 5.8.9.** Derive an expression relating the constant volume heat capacity at constant \mathcal{H}_0 to that at constant \mathcal{M} .

5.9 Adiabatic Diamagnetization and Transitions to Superconductivity

We discuss the further manipulation of Eq. (5.8.19) via Eq. (5.8.23) in the context of *adiabatic demagnetization*. The experiment consists in allowing a material to equilibrate with surroundings held in a liquid helium bath maintained at a low vapor pressure corresponding to roughly 0.3 K. The sample is subjected to an intense magnetic field and is then adiabatically isolated, after which the external field is switched off. As repeatedly emphasized, any change of state under such conditions incurs a change of temperature, whose difference is determined by Eqs. (5.8.19) and (5.8.23). With $\mathcal{M} = A_1 \mathcal{H}_0 / T$, as before, we find that

$$(dT/T)_{S, V} = [A_2 \mathcal{H}_0 / (A_1 + A_2 \mathcal{H}_0^2)] \cdot d\mathcal{H}_0|_{S, V}, \quad (5.9.1a)$$

which is recast in the form

$$d \ln T|_{S, V} = (A_1 / A_2 + \mathcal{H}_0^2)^{-1} \mathcal{H}_0 \cdot d\mathcal{H}_0|_{S, V}. \quad (5.9.1b)$$

On integrating from an initial value (T_i, \mathcal{H}_0) to a final value $(T_f, 0)$ at constant S and V , we find for the class of materials that is subject to Eq. (5.8.23),

$$(T_f/T_i) = [1 + \mathcal{H}_0^2 A_2/A_1]^{-1/2}, \quad (5.9.2)$$

which is the solution to the problem. One concludes that for a Curie-type paramagnetic material with $\mathcal{M} = A_1 \mathcal{H}_0/T$, the above demagnetization lowers the temperature since $\mathcal{H}_0^2 A_2/A_1$ is positive. The larger the effects, the greater the *Curie constant* A_2 and the smaller the heat capacity density $C'_{V,\mathcal{H}_0} \sim A_1$. These relations have been experimentally verified.

One may also determine the amount of heat transferred in this process: start with Eq. (5.7.15), set $dV=0$, exchange magnetic for electric field variables, and introduce the heat capacity via $C_{V,\mathcal{H}_0}/T = (\partial S/\partial T)_{V,\mathcal{H}_0}$. Then use the Maxwell relation, line k of Table 5.8.I, and multiply both sides by T . This yields

$$TdS|_V = C_{V,\mathcal{H}_0} dT|_V = T \int_V d^3\mathbf{r} (\partial \mathcal{M}/\partial T)_{V,\mathcal{H}_0} \cdot d\mathcal{H}_0|_V. \quad (5.9.3)$$

If now the field is changed in a reversible manner at constant temperature, we obtain

$$\delta Q_r|_{T,V} = T \int_V d^3\mathbf{r} (\partial X_0/\partial T)_{V,\mathcal{H}_0} \mathcal{H}_0 \cdot d\mathcal{H}_0|_{V,T}. \quad (5.9.4a)$$

Since the partial derivative is negative, a rise in magnetic field at constant T will result in a transfer of heat from the sample to the surroundings. On assuming that the integrand does not vary with position within the sample, we obtain

$$Q_r|_{T,V} = -VA_1 \mathcal{H}_0^2/2T. \quad (5.9.4b)$$

Transitions to the Superconducting State

The preceding material may be used to characterize the thermodynamics of transitions from the normal to the superconducting state. This transformation takes place for a limited class of materials at a particular temperature T_c , currently below 140 K. For soft superconductors of type I, this state is marked by a complete disappearance of electrical resistivity and by the fact that at moderate values, the magnetic induction $\mathcal{B} = \mathcal{M} + 4\pi\mathcal{H}$ vanishes within the bulk of the sample, so that for such materials $\mathcal{M} = -4\pi\mathcal{H}$. However, as the field is increased, a critical magnetic field \mathcal{H}_c is reached beyond which the material reverts back to its normal state. In first approximation, \mathcal{H}_c depends only on temperature according to the relation

$$\mathcal{H}_c = \mathcal{H}_1 (1 - T^2/T_c^2), \quad (5.9.5)$$

where T_c is the normal-superconducting transition temperature in zero field. The transformation for fixed T and \mathcal{H}_1 is an ordinary phase transformation that is most easily handled by returning to the relation $dG = -SdT + VdP_m - \int_V d^3\mathbf{r} \mathcal{M} \cdot d\mathcal{H}_0$. At constant $P_m \approx P$, we characterize the equilibrium between the normal (n) and superconducting (s) states by the condition $dG_s|_{P_m} = dG_n|_P$, so that

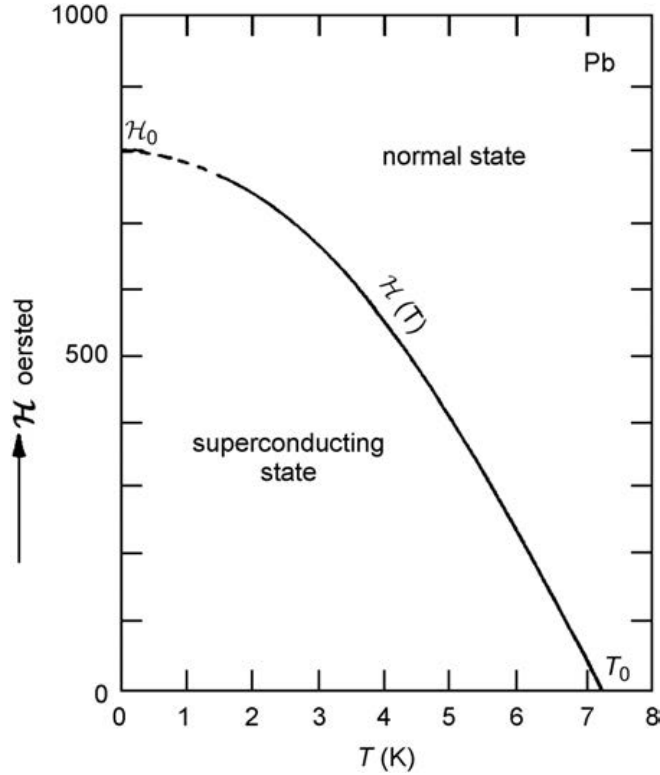


FIGURE 5.9.1

Variation of \mathcal{H}_c with temperature for elemental lead in the superconducting and normal state.

$$-S_n dT - \int_V d^3\mathbf{r} \mathcal{M}_n \cdot d\mathcal{H}_0 = -S_s dT - \int_V d^3\mathbf{r} \mathcal{M}_s \cdot d\mathcal{H}_0 \quad (\mathcal{H}_0 = \mathcal{H}_c; \quad P_m \approx P). \quad (5.9.6a)$$

For simplicity, replace the integral $\int_V d^3\mathbf{r} \mathcal{M}$ by $V\overline{\mathcal{M}}$ and rearrange the above relation to read

$$-(\partial\mathcal{H}_c/\partial T)_P = (S_n - S_s)/(V\overline{\mathcal{M}}_n - V\overline{\mathcal{M}})^{-1}. \quad (5.9.6b)$$

If the magnetization of the material in its normal state is essentially zero, and on setting $\overline{\mathcal{M}}_s = -\mathcal{H}_c/4\pi$, one obtains

$$S_n - S_s = -(V/4\pi)[\mathcal{H}_c \cdot (\partial\mathcal{H}_c/\partial T)_P]. \quad (5.9.7)$$

Several points are to be noted. (i) First, the obvious analogy to the Clausius–Clapeyron equation. (ii) According to the third law, as $T \rightarrow 0$, the entropy of any material must reach a minimum value with zero slope; hence, $(\partial\mathcal{H}_c/\partial T)_P \rightarrow 0$ as well (cf. Figure 5.9.1). (iii) Experimentally it is found that $(\partial\mathcal{H}_c/\partial T)_P < 0$; therefore, in a magnetic field, the superconducting state has a lower entropy than does the normal state. (iv) The enthalpy of the transition is given by $\Delta H = T(S_n - S_s)$; this quantity vanishes for $\mathcal{H}_c = 0$.

Equation (5.9.7) may be differentiated with respect to T and then multiplied by T ; one obtains an equation for the heat capacity as follows:

$$C_s - C_n = \left(\frac{VT}{4\pi}\right) \left(\frac{\partial}{\partial T}\right) \left\{ \mathcal{H}_c \cdot \left[\left(\frac{\partial \mathcal{H}_c}{\partial T}\right)_P \right] \right\} = \left(\frac{VT}{4\pi}\right) \left[\mathcal{H}_c \left(\frac{\partial^2 \mathcal{H}_c}{\partial T^2}\right)_P + \left(\frac{\partial \mathcal{H}_c}{\partial T}\right)_P^2 \right]. \quad (5.9.8)$$

At $T = T_c$, the condition $\mathcal{H}_c = 0$ holds; for this case,

$$\left(\frac{\partial \mathcal{H}_c}{\partial T}\right)_{P, T=T_c} = \left[(4\pi/VT_c)(C_s - C_n)_{T_c} \right]^{1/2}. \quad (5.9.9)$$

The above expression is known as *Rutger's equation*; it determines the slope of the plots of \mathcal{H}_c vs T at $T = T_c$. This forms the basis of the plot shown in Figure 5.9.1.

Last, we may integrate Eq. (5.9.8) to obtain

$$\begin{aligned} \int_0^{T_c} (C_s - C_n) dT &= \frac{V}{4\pi} \int_{\mathcal{H}_0}^0 T \frac{d}{dT} \left[\mathcal{H}_c \cdot \left(\frac{\partial \mathcal{H}_c}{\partial T}\right)_P \right] dT = \frac{V}{4\pi} T \mathcal{H}_c \cdot \left(\frac{\partial \mathcal{H}_c}{\partial T}\right)_P \Big|_0^{T_c} \\ &\quad - \frac{V}{4\pi} \int_{\mathcal{H}_0}^0 \left[\mathcal{H}_c \cdot \left(\frac{\partial \mathcal{H}_c}{\partial T}\right)_P \right] dT = \frac{V \mathcal{H}_0^2}{8\pi}, \end{aligned} \quad (5.9.10)$$

where the term on the right, top line, vanishes at $T = 0$ and $T = T_c$. The above expression may be inverted to read

$$\mathcal{H}_0 = \left[\frac{8\pi}{V} \int_0^{T_c} (C_s - C_n) dT \right]^{1/2}, \quad (5.9.11)$$

which serves as a means of finding the maximum value of the critical field.

5.10 Thermodynamic Characterization of Anisotropic Media

Deformations Characterized by Tensors of Second Rank

We begin here a study of thermodynamic properties of anisotropic media that closely follows the presentation by J.F. Nye.¹ The introductory material is straightforward, but after that the details get to be rather messy. At first reading, you may wish to skip parts of this section.

By way of introduction, consider Ohm's law for isotropic media in standard form $\mathbf{J} = \sigma \mathbf{E}$, which relates the current density via the conductivity to the electric field that is externally imposed. In standard component notation, this takes the form $J_i = \sigma E_i$, $i = 1, 2, 3$, where the numerals refer respectively to the mutually orthogonal Ox , Oy , and Oz Cartesian axes. For simplicity, the vector may be made to coincide with the Ox axis. In isotropic media, the current flow direction coincides with that of the electric field.

By contrast, in anisotropic media, the current density becomes direction-dependent. For a proper description that fits all cases, the above relation must be generalized to read

$$\begin{aligned}
J_1 &= \sigma_{11}\mathcal{E}_1 + \sigma_{12}\mathcal{E}_2 + \sigma_{13}\mathcal{E}_3 \\
J_2 &= \sigma_{21}\mathcal{E}_1 + \sigma_{22}\mathcal{E}_2 + \sigma_{23}\mathcal{E}_3 \\
J_3 &= \sigma_{31}\mathcal{E}_1 + \sigma_{32}\mathcal{E}_2 + \sigma_{33}\mathcal{E}_3,
\end{aligned} \tag{5.10.1}$$

where the σ_{ij} forms the components of a tensor of second rank that specifies the anisotropic electrical conductivity. Thus, in anisotropic media, every component of the electric field vector contributes to the magnitude of each component of the current density. An equivalent formulation is provided in matrix notation:

$$\begin{vmatrix} J_1 \\ J_2 \\ J_3 \end{vmatrix} = \begin{vmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{vmatrix} \begin{vmatrix} \mathcal{E}_1 \\ \mathcal{E}_2 \\ \mathcal{E}_3 \end{vmatrix}. \tag{5.10.2}$$

We note that line i of Eq. (5.10.1) may be rewritten as $J_i = \sum_{j=1}^3 \sigma_{ij}\mathcal{E}_j$ ($i = 1, 2, 3$). For simplicity, we now introduce the Einstein summation convention; we set $J_i = \sigma_{ij}\mathcal{E}_j$, where the *repeated dummy index* j on the right indicates a *summation*, currently over all three ($j = 1, 2, 3$) values; by contrast, ($i = 1, 2, 3$) is the *free index*. This convention will be followed in all subsequent derivations; however, do remember that many of the simple expressions shown below actually involve a set of extensive summations.

Analogous ideas apply to thermal conductivity. In isotropic media, the rate of heat flow is governed by Fourier's law in the form $\mathbf{J}_Q = -k\nabla T$, where \mathbf{J}_Q is the heat flux vector, κ is the thermal conductivity of the sample, which multiplies the externally applied temperature gradient. Again, the directions of the heat flux and the temperature gradients coincide.

In anisotropic media, this relation is replaced by

$$J_i^Q = -\kappa_{ij}(\partial T / \partial x_j) \quad (\text{repeated index notation; } i, j = 1, 2, 3), \tag{5.10.3}$$

when the temperature gradient and the direction of the heat flux do not coincide. Again, each component of the heat flux vector depends on all three components of the temperature gradient vector.

Deformation Effects in Anisotropic Media; Second Rank Tensors; Application of Stresses

The above sets the stage for the general consideration of deformations in anisotropic media. Attention is directed to Figure 5.10.1, which shows an elemental cube to which an external stress, i.e. a force per unit area, has been applied. In the most general case, this stress acts along an arbitrary direction and must therefore be resolved into the indicated components on each of the three faces that are perpendicular to the indicated $Ox \equiv O_1, Oy \equiv O_2, Oz \equiv O_3$ Cartesian axes that coincide with the cube edges. The stress components are designated by σ_{ij} (obviously, not to be confused with the components of the electrical conductivity tensor introduced above), where the index j relates to the particular face that is normal to the positive O_j direction. The index i coincides with the indicated O_i direction. The σ_{ji} and σ_{ij} entries are known as *normal* and *shear components*, respectively. According to the convention generally—but not universally—adopted, positive and negative values of the normal components correspond to tensile and compressive stresses. Except in the presence of electric and magnetic fields, when static equilibrium conditions prevail, one finds that $\sigma_{ij} = \sigma_{ji}$

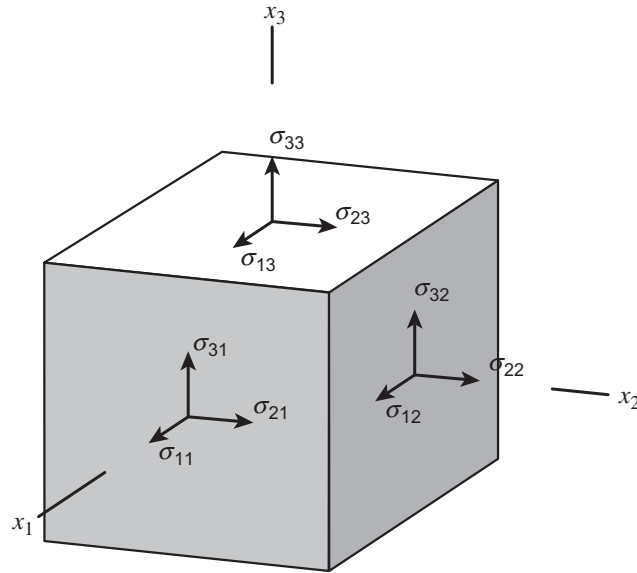


FIGURE 5.10.1

Illustration showing the various stress components acting on a cube. Reproduced from J.F. Nye, *Physical Properties of Crystals*, Clarendon Press, 1957; by permission of Oxford University Press.

Response to Stresses; Deformations in Two Dimensions

We now take up the response of a body to the imposition of external stresses. The starting point here is Hooke's law, which is generally applicable for small imposed stresses σ that induce a linear response. In isotropic bodies, the response is a strain $e = \Delta l/l$ that represents the fractional change in length of the material. For isotropic substances, Hooke's law thus assumes the form $e = s\sigma$, where s , termed the *compliance*, indicates the degree of response to the applied stress.

The situation in anisotropic media is much more complicated. As usual, we limit our considerations to "small" departures from equilibrium. We first investigate the shift in position of a point P located on a sheet, in response to the application of a small stress. Relative to the Cartesian axes Ox_1 and Ox_2 , the displacement of P from (x_1, x_2) to $(x_1 + u_1, x_2 + u_2)$ with $u_i \ll x_i$, requires the specification of the following four strain components for the sheet:

$$e_{11} = \partial u_1 / \partial x_1, \quad e_{12} = \partial u_1 / \partial x_2, \quad e_{21} = \partial u_2 / \partial x_1, \quad e_{22} = \partial u_2 / \partial x_2; \quad \text{or} \quad e_{ij} = \partial u_i / \partial x_j \quad (i, j = 1, 2), \quad (5.10.4)$$

where the dimensionless e_{ij} are small compared to unity.

The resulting displacements are shown in Figure 5.10.2. In general, the shift from P to P' involves the alterations (note the extensions and shift in direction of the initial vector components)

$$\Delta u_1 = (\partial u_1 / \partial x_1) \Delta x_1 + (\partial u_1 / \partial x_2) \Delta x_2; \quad \Delta u_2 = (\partial u_2 / \partial x_1) \Delta x_1 + (\partial u_2 / \partial x_2) \Delta x_2. \quad (5.10.5)$$

Consider now the shift in a PQ_1 vector which is initially aligned with the Ox_1 axis. Then, in Eq. (5.10.5), we may set $\Delta x_2 = 0$, so that $\Delta u_1 = e_{11} \Delta x_1$ and $\Delta u_2 = e_{21} \Delta x_1$. The resulting distortion is shown in the elevated position of the diagram. $P'Q'_1$ has now been shifted away from the Ox_1 axis. A similar situation obtains for the vector PQ_2 initially aligned with the Ox_2 direction; $P'Q'_2$ now veers away from the x_2 axis. Clearly, e_{11} measures the extension of PQ_1 per unit length along the Ox_1

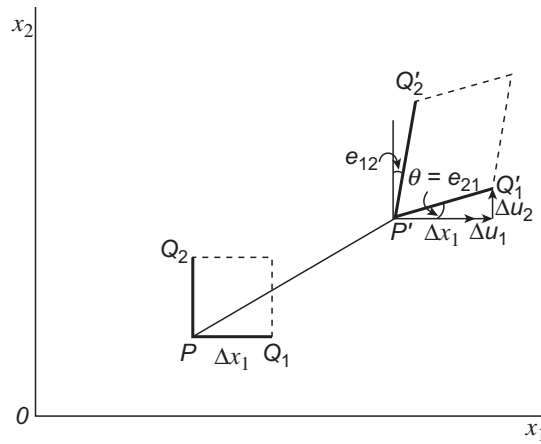


FIGURE 5.10.2

Strain components in a two-dimensional configuration. Reproduced from J.F. Nye, *Physical Properties of Crystals*, Clarendon Press, 1957; by permission of Oxford University Press.

direction, while e_{21} represents the angle generated by the infinitesimal counter-clockwise rotation of the PQ_1 vector so as to coincide with the position of the $P'Q'_1$ vector. That is, the angle of rotation is specified by $\tan \theta \approx \theta = \Delta u_2 / (\Delta x_1 + \Delta u_2) \approx \Delta u_2 / \Delta x_1 = e_{21}$, where the approximations hold for small displacements. Similarly, one may show that e_{22} and e_{12} represent, respectively, the extension per unit length of PQ_2 along the Ox_2 direction and the clockwise angle of rotation of the PQ_2 vector.

One last point: there is a difficulty with above representation because it includes configurational changes that arise from pure rotations of the rigid body; these are of no direct interest in a study of deformations. We eliminate this contribution by noting that any second-rank tensor may be reexpressed as the sum of a symmetric and of an antisymmetric component: we therefore introduce two new coordinates

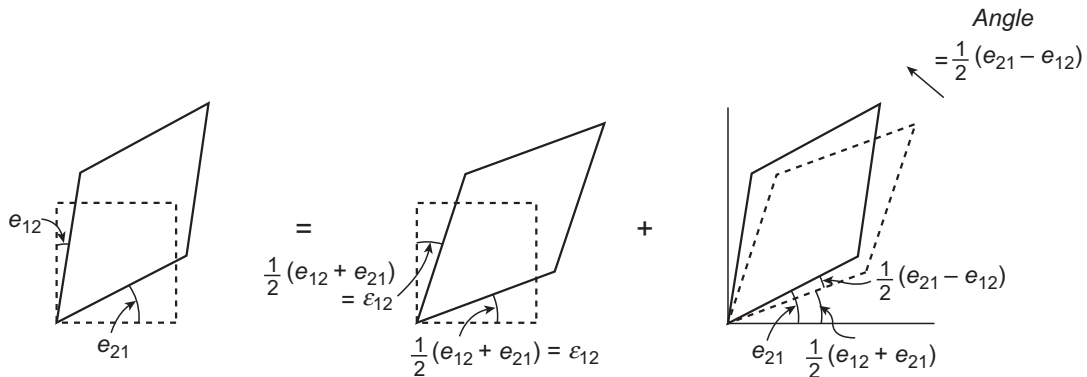


FIGURE 5.10.3

General two-dimensional deformations consisting of a strain, followed by a rotation. Reproduced from J.F. Nye, *Physical Properties of Crystals*, Clarendon Press, 1957; by permission of Oxford University Press.

$$e_{ij} = \varepsilon_{ij} + \varpi_{ij}; \quad \varepsilon_{ij} \equiv (e_{ij} + e_{ji})/2 = \varepsilon_{ji}; \quad \varpi_{ij} \equiv (e_{ij} - e_{ji})/2 = -\varpi_{ji}. \quad (5.10.6)$$

ε_{ij} and ϖ_{ij} as defined here are obviously entries in a symmetric and antisymmetric tensor, respectively.

The further discussion is based on a careful examination of Figure 5.10.3; on the left is shown a dashed square figure which has been deformed into a tilted solid diamond shape. This operation may be viewed as a superposition of the two processes depicted on the right: the first shows the diamond at a shallower tilting angle $\varepsilon_{12} = (e_{12} + e_{21})/2$. The second reproduces the central diamond figure as a dashed shape and indicates the need to apply a pure rotation through an additional angle $(e_{21} - e_{12})/2$, so as to turn the dashed figure into its final solid shape at a position that coincides with the left diagram. For an alternative justification of these statements, see below. By discarding the second operation, we are left with the deformation process of interest. In brief, we associate strain effects solely with the symmetric part of the tensor, i.e. with

$$\begin{vmatrix} \varepsilon_{11} & \varepsilon_{12} \\ \varepsilon_{21} & \varepsilon_{22} \end{vmatrix} = \begin{vmatrix} e_{11} & (e_{12} + e_{21})/2 \\ (e_{12} + e_{21})/2 & e_{22} \end{vmatrix}. \quad (5.10.7)$$

Deformations in Three Dimensions; Tensors of Rank Four

The above may now be extended to three dimensions. We then deal with a nine-component tensor with entries

$$e_{ij} = (\partial u_i / \partial x_j) \quad (i, j = 1, 2, 3). \quad (5.10.8)$$

Here the e_{ij} are the extensions per unit length parallel to the Ox_j axis; e_{21} and e_{12} represent, respectively, the rotation angles about the Ox_3 axis toward Ox_2 and toward Ox_1 of a line element originally parallel to Ox_1 and Ox_2 . In a pure rotation element about an arbitrary axis, the change in position of the displacement vector u_i is orthogonal to the starting vector x_j ; the dot product between these quantities thus vanishes. In terms of components (with the Einstein summation convention), $u_i x_j$ vanishes, whence $e_{ij} x_i x_j = 0$. This sum can vanish only if all e_{ij} vanish. Hence, we require $e_{ii} = 0$ and all $e_{ij} = -e_{ji}$, these being precisely the conditions that render the e tensor antisymmetric. In accord with our earlier discussion, we therefore link the deformations of solids solely to the symmetric tensor

$$\begin{vmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{vmatrix} = \begin{vmatrix} e_{11} & (e_{12} + e_{21})/2 & (e_{13} + e_{31})/2 \\ (e_{12} + e_{21})/2 & e_{22} & (e_{23} + e_{32})/2 \\ (e_{13} + e_{31})/2 & (e_{23} + e_{32})/2 & e_{33} \end{vmatrix}, \quad (5.10.9)$$

and will henceforth deal with the individual ε_{ij} . The diagonal components form the *tensile strains*, while the off-diagonal components measure the *shear strains* arising from the imposed stress.

Strains

We next examine the *response* of the anisotropic medium to the applied stress. In the general case, if a homogeneous stress is applied, the resulting homogeneous strain ε_{ij} —in the limit of Hooke's law—depends linearly on all nine σ_{ij} components of the stress tensor of the same form as displayed in Eq. (5.10.2). The relation between stress and strain is encoded in the compliance tensor. As a typical example, note the following relationship:

$$\begin{aligned} \varepsilon_{11} = & s_{1111}\sigma_{11} + s_{1112}\sigma_{12} + s_{1113}\sigma_{13} + s_{1121}\sigma_{21} + s_{1122}\sigma_{22} + s_{1123}\sigma_{23} \\ & + s_{1131}\sigma_{31} + s_{1132}\sigma_{32} + s_{1133}\sigma_{13}, \end{aligned} \quad (5.10.10)$$

with similar expressions for the remaining ε_{ij} . Here the S_{ijkl} are entries in the *compliance tensor* s . Clearly, we are now dealing with a fourth rank tensor, involving a grand total of 81 entries. More generally, Hooke's law for anisotropic media assumes the linearized Einstein form for nine equations, each involving nine summed terms:

$$\varepsilon_{ij} = s_{ijkl}\sigma_{kl} \quad (i, j, k, l = 1, 2, 3). \quad (5.10.11)$$

It is equally possible mathematically to invert the above relations to express stresses as a response to strains by writing

$$\sigma_{ij} = s_{ijkl}\varepsilon_{kl}, \quad (5.10.12)$$

where the c_{ijkl} are components of the *stiffness tensor*. Physical constraints show that in general $s_{ijkl} = s_{jilk}$ and $s_{ijkl} = s_{jikl}$ as well as $c_{ijkl} = c_{jilk}$ and $c_{ijkl} = c_{jikl}$; hence, only 36 of the 81 tensor entries are independent.

Obviously, it would be very helpful to simplify the notation. This is accomplished by introducing a single subscript index running from one to six according to the following conventions that are introduced for general notational convenience:

$$\begin{vmatrix} \sigma_{11} & \sigma_{12} & \sigma_{31} \\ \sigma_{12} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{23} & \sigma_{33} \end{vmatrix} \rightarrow \begin{vmatrix} \sigma_1 & \sigma_6 & \sigma_5 \\ \sigma_6 & \sigma_2 & \sigma_4 \\ \sigma_5 & \sigma_4 & \sigma_3 \end{vmatrix}; \quad \begin{vmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{31} \\ \varepsilon_{12} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{23} & \varepsilon_{33} \end{vmatrix} \rightarrow \begin{vmatrix} \varepsilon_1 & \varepsilon_6/2 & \varepsilon_5/2 \\ \varepsilon_6/2 & \varepsilon_2 & \varepsilon_4/2 \\ \varepsilon_5/2 & \varepsilon_4/2 & \varepsilon_3 \end{vmatrix}. \quad (5.10.13a)$$

with the following additional abbreviations for the four compliance and stiffness subscripts: the first two subscripts are abbreviated into a single number running from 1 to 6, and the last two are similarly abbreviated according to the scheme shown in Eq. (5.10.13a):

$$11 \rightarrow 1; \quad 22 \rightarrow 2; \quad 33 \rightarrow 3; \quad 23, 32 \rightarrow 4; \quad 31, 13 \rightarrow 5; \quad 12, 21 \rightarrow 6. \quad (5.10.13b)$$

Additionally, the following numerical factors are introduced for later notational convenience:

$$\begin{aligned} s_{ijkl} = s_{mn} \text{ when } m, n = 1, 2, 3; \quad s_{ijkl} = s_{mn}/2 \text{ when either} \\ m \text{ or } n = 4, 5, 6; \text{ and } s_{ijkl} = s_{mn}/4 \text{ when both } m, n = 4, 5, 6. \end{aligned} \quad (5.10.13c)$$

For example, Eq. (5.10.11) now becomes $\varepsilon_1 = s_{11}\sigma_1 + s_{12}\sigma_2 + s_{13}\sigma_3 + 2s_{16}\sigma_6/2 + 2s_{15}\sigma_5/2 + 2s_{14}\sigma_4/2$, or, in abbreviated form, $\varepsilon_1 = s_{1j}\sigma_j$; similarly, $\varepsilon_4/2 = s_{41}\sigma_1/2 + s_{42}\sigma_2/2 + s_{43}\sigma_3/2 + 2s_{46}\sigma_6/4 + 2s_{45}\sigma_5/4 + 2s_{44}\sigma_4/4$, or, in abbreviated form: $\varepsilon_4 = s_{4j}\sigma_j$. Thus,

$$\varepsilon_i = s_{ij}\sigma_j \quad \text{or} \quad \sigma_i = c_{ij}\varepsilon_j. \quad (i, j = 1, 2, \dots, 6) \quad (5.10.13d)$$

It turns out that for the stiffness entries, no numerical factors need be introduced.

In the above notational scheme, we therefore have the following matrix entries for the compliance matrix that links the deformation relation (in Einstein form) to the applied stress, $\varepsilon_i = s_{ij}\sigma_j$:

$$|s_{ij}| = \begin{vmatrix} s_{11} & s_{12} & s_{13} & s_{14} & s_{15} & s_{16} \\ s_{21} & s_{22} & s_{23} & s_{24} & s_{25} & s_{26} \\ s_{31} & s_{32} & s_{33} & s_{34} & s_{35} & s_{36} \\ s_{41} & s_{42} & s_{43} & s_{44} & s_{45} & s_{46} \\ s_{51} & s_{52} & s_{53} & s_{54} & s_{55} & s_{56} \\ s_{61} & s_{62} & s_{63} & s_{64} & s_{65} & s_{66} \end{vmatrix}, \quad (5.10.14)$$

with a similar set of entries for $|c_{ij}|$.

The above relations are presented in their most general form. Considerable simplifications are achieved by taking account of crystal symmetry; depending on the degree of symmetry, many entries are found to vanish or to be related numerically to other entries. This topic requires detailed considerations that are beyond the purview of the present discussion. Consult the Nye, (Oxford, 1957) or textbooks on crystallography for an introduction to this topic.

Link to Thermodynamics

We now provide a preliminary link to thermodynamics: consider a cubic crystal in unstrained form that is subjected to a small homogeneous stress; the resulting strain is specified by the symmetric tensor components ε_i ($i = 1, 2, \dots, 6$) of Eq. (5.10.13a). The corresponding element of work is then represented as usual by the generalized force component multiplying the corresponding differential of the displacement response, as in Eq. (5.10.13d):

$$dW = \sigma_i d\varepsilon_i \quad (i = 1, 2, \dots, 6). \quad (5.10.15)$$

As established in Eq. (1.9.8a), elements of work performed under isothermal and reversible conditions are identical with the element of the Helmholtz function, dA . Thus, when Hooke's law is obeyed under isothermal conditions, we may introduce Eq. (5.10.13d) to write

$$dA_\varepsilon = c_{ij} \varepsilon_j d\varepsilon_i. \quad (5.10.16)$$

It follows that $\partial^2 A / \partial \varepsilon_j \partial \varepsilon_i = c_{ij} = \partial^2 A / \partial \varepsilon_i \partial \varepsilon_j = c_{ji}$; also, $s_{ij} = s_{ji}$; whence the number of independent stiffness constants and compliances is reduced from 36 to 21. We may then integrate Eq. (5.10.16) to obtain the work or isothermal free energy per unit volume needed to produce the strain ε_j , i.e. the *strain (free) energy density*, as

$$A_\varepsilon = (1/2) c_{ij} \varepsilon_i \varepsilon_j. \quad (5.10.17a)$$

It is now pertinent to introduce a related Helmholtz free energy defined by $A_\sigma = E - \sigma_{ij} \varepsilon_{ij} - TS$, where the central term represents a sum of nine separate terms. Then, its differential reads

$$dA_\sigma = -\varepsilon_{ij} d\sigma_{ij} - SdT, \quad (5.10.17b)$$

so that by the conventional Maxwell construction, we arrive at

$$\left(\frac{\partial \varepsilon_{ij}}{\partial T} \right)_\sigma = \left(\frac{\partial S}{\partial \sigma_{ij}} \right)_T. \quad (5.10.17c)$$

Piezoelectric Effects; Electric Polarizations Arising from Stress; Tensors of Third Rank

Here we deal with the response of certain classes of anisotropic crystals to the imposition of a homogeneous stress, as a result of which they display electric polarization effects. Physically, this arises because, in the unstressed state, such materials display dipole moments in distinct orientations, governed by the crystal symmetry, that cancel each other out. When a stress is applied, such a crystal deforms and the original cancellation no longer holds. This response is known as the *piezoelectric effect*. As an example, let a uniaxial tensile stress σ be applied along a dyadic axis of a quartz crystal; this produces an electric moment per unit volume (or, equivalently, a polarization charge per unit cross-section) \mathcal{P} whose magnitude is specified by

$$\mathcal{P} = d\sigma, \quad (5.10.18)$$

where d is the *piezoelectric modulus*. A changeover from tensile to an equal compressive stress reverses the direction of the polarization. \mathcal{P} , being a vector, requires the specification of three components, whereas the second-rank tensor d involves nine components. Each component of polarization \mathcal{P}_i in general depends linearly on all components of σ as indicated by the following example:

$$\begin{aligned} \mathcal{P}_1 &= d_{111}\sigma_{11} + d_{112}\sigma_{12} + d_{113}\sigma_{13} + d_{121}\sigma_{21} + d_{122}\sigma_{22} + d_{123}\sigma_{23} \\ &\quad + d_{131}\sigma_{31} + d_{132}\sigma_{32} + d_{133}\sigma_{33} = d_{1jk}\sigma_{jk}, \end{aligned} \quad (5.10.19a)$$

or, more generally,

$$\mathcal{P}_i = d_{ijk}\sigma_{jk}, \quad (5.10.19b)$$

The d_{ijk} form elements of a third-rank tensor; in general, $d_{ijk} = d_{ikj}$. The 27 elements require a three-dimensional representation. In the two dimensions of the printed word, this is achieved by superposition of three two-dimensional layers in the following order, based on d_{ijk} :

First layer $i = 1$			Second layer $i = 2$			Third layer $i = 3$		
d_{111}	d_{112}	d_{113}	d_{211}	d_{212}	d_{213}	d_{311}	d_{312}	d_{313}
(d_{112})	d_{122}	d_{123}	(d_{212})	d_{222}	d_{223}	(d_{312})	d_{322}	d_{323}
(d_{113})	(d_{123})	d_{133}	(d_{213})	(d_{223})	d_{233}	(d_{313})	(d_{323})	d_{333}

(5.10.19c)

The notation for the 18 independent entries may be simplified, as was done previously in accordance with Eqs. (5.10.13), while introducing numerical factors that simplify the subsequent operations. We thus set up the following arrays:

First layer $i = 1$			Second layer $i = 2$			Third layer $i = 3$		
d_{11}	$\frac{d_{16}}{2}$	$\frac{d_{15}}{2}$	d_{21}	$\frac{d_{26}}{2}$	$\frac{d_{25}}{2}$	d_{31}	$\frac{d_{36}}{2}$	$\frac{d_{35}}{2}$
$(\frac{d_{16}}{2})$	d_{12}	$\frac{d_{14}}{2}$	$(\frac{d_{26}}{2})$	d_{22}	$\frac{d_{24}}{2}$	$(\frac{d_{36}}{2})$	d_{32}	$\frac{d_{34}}{2}$
$(\frac{d_{15}}{2})$	$(\frac{d_{14}}{2})$	d_{13}	$(\frac{d_{25}}{2})$	$(\frac{d_{24}}{2})$	d_{23}	$(\frac{d_{35}}{2})$	$(\frac{d_{34}}{2})$	d_{33}

(5.10.19d)

A corresponding change in the suffix notation for the stress components follows the same scheme as in Eq. (5.8.13). We thus specify the first component of the polarization vector as

$$\mathcal{P}_1 = d_{11}\sigma_1 + d_{12}\sigma_2 + d_{13}\sigma_3 + d_{14}\sigma_4 + d_{15}\sigma_5 + d_{16}\sigma_6 = d_{1j}\sigma_j. \quad (5.10.20)$$

The Converse Piezoelectric Effect

We now consider the converse of the above, namely the distortion suffered by an anisotropic crystal as a response to an externally applied electric field \mathcal{E} , which is known as the *converse piezoelectric effect*. Here the imposition of an electric field creates a unique alignment direction for the dipoles that eliminates the cancellation effect described earlier. As a result, the crystal deforms. The coefficients relating the strain to the electric field are the same as those that connect the polarization to the stress in the direct effect. The proof will be provided later by noncircular arguments. We thus characterize the present linear dependence by the relation

$$\varepsilon_{jk} = d_{ijk}\mathcal{E}_i. \quad (5.10.21)$$

The rather complex suffix notation is abbreviated in the manner of Eqs. (5.10.13), such that, for example, $\varepsilon_{11} = d_{111}\mathcal{E}_1 + d_{211}\mathcal{E}_2 + d_{311}\mathcal{E}_3$ now reads $\varepsilon_1 = d_{11}\mathcal{E}_1 + d_{21}\mathcal{E}_2 + d_{31}\mathcal{E}_3$, while $\varepsilon_{23} = d_{123}\mathcal{E}_1 + d_{223}\mathcal{E}_2 + d_{323}\mathcal{E}_3$, becomes $\varepsilon_4/2 = d_{14}\mathcal{E}_1/2 + d_{24}\mathcal{E}_2/2 + d_{34}\mathcal{E}_3/2$. Generally, therefore,

$$\varepsilon_j = d_{ij}\mathcal{E}_i. (i = 1, 2, 3; j = 1, 2, \dots, 6). \quad (5.10.22)$$

Once more, many of the above-mentioned components vanish or are related to one another when the theory is applied to crystals that contain elements of symmetry.

Electric Response

The above presentation may be summarized by

$$\mathcal{P}_i = d_{ijk}\sigma_{jk}. \quad (5.10.23)$$

However, it is more appropriate to take the electric displacement vector \mathcal{D} as the quantity that responds to the imposition of an electric field \mathcal{E} ; here, $\mathcal{D} = \mathcal{E} + 4\pi\mathcal{P}$ specifies the response of the medium to the externally applied electric field as well as to the induced polarization. Henceforth, this is the quantity that will be used in the subsequent analysis. Clearly, at constant \mathcal{E} , the differentials of \mathcal{D} and \mathcal{P} are identical.

Reference

5.10.1 J.F. Nye, *Physical Properties of Crystals* (Clarendon Press, Oxford, 1957).

5.11 Thermodynamic Properties of Anisotropic Media

A complete treatment of thermodynamic properties of anisotropic media would take us too far afield; the rather abbreviated presentation offered below serves as an introduction on which you can then build. A more extensive presentation may be found in Nye, (Oxford, 1957).

Thermoelastic Properties

Here we present a simple example for the coupling of two effects, namely, the interaction between thermal manipulations and the elastic properties of an anisotropic crystal. Let T and the nine stress components σ_{ij} be the independent variables, and S and the strain components ε_{ij} as their dependent counterparts. In conformity with the discussion of Section 2.2, and with the more elaborate establishment of phenomenological equations in Section 6.3, we postulate that the joint action of the thermal and elastic forces may be described by the set of linear phenomenological equations per unit volume of the form

$$\begin{aligned} d\varepsilon_{ij} &= \left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}} \right)_T d\sigma_{kl} + \left(\frac{\partial \varepsilon_{ij}}{\partial T} \right)_\sigma dT && \text{(elasticity + thermal expansion)} \\ dS &= \left(\frac{\partial S}{\partial \sigma_{kl}} \right)_T d\sigma_{kl} + \left(\frac{\partial S}{\partial T} \right)_\sigma dT && \text{(piezocaloric + heat capacity).} \end{aligned} \quad (5.11.1a)$$

Attention is directed to the associated nomenclature. The equations display the joint action—i.e. the linear superposition—of stress and temperature variations on the strain and entropy change. The above is deceptively simple; the first term of the top equation really represents the sum,

$$\left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}} \right)_T d\sigma_{kl} = \left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{11}} \right) d\sigma_{11} + \left(\frac{\partial \varepsilon_{ij}}{\partial \sigma_{12}} \right) d\sigma_{12} + \cdots, \quad (5.11.1b)$$

in which temperature and all stress components except for the one being differentiated are to be held constant. The subscript σ implies that all such components of type Eq. (5.11.1b) are held fixed. Note further that with $i, j = 1, 2, 3$, we really have nine equations in place of the first row of Eq. (5.11.1a).

When $dT = 0$, the $(\partial \varepsilon_{ij} / \partial \sigma_{kl})$ represents the isothermal elastic compliances of the crystal; setting $d\sigma_{kl} = 0$ shows that $(\partial \varepsilon_{ij} / \partial T)$ is nothing other than the thermal expansion coefficient per unit volume. The product $T(\partial S / \partial \sigma_{kl})$ yields the heat produced when a crystal is stressed isothermally. Note that on account of Eqs. (5.10.16) and (5.10.17c), the off-diagonal components are equal—a prediction based on thermodynamics that may be checked by experiment.

Interactions between Thermal, Electrical, and Elastic Properties

We now extend the above discussion to include electrical properties via the generalization of Eq. (5.11.1a), choosing σ_{ij} , \mathcal{E}_i , and T as independent variables, and ε_{ij} , \mathcal{D} , and S as dependent variables. This attends to the interactions between stress, electric fields, and thermal effects, whose response is governed by strain, electric displacement, and entropy, respectively. Assuming, as usual, a linear superposition of these inputs, the phenomenological relations read as follows:

$$\begin{aligned}
d\epsilon_{ij} &= \left(\frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} \right)_{\epsilon, T} d\sigma_{kl} + \left(\frac{\partial \epsilon_{ij}}{\partial \mathcal{E}_k} \right)_{\sigma, T} d\mathcal{E}_k + \left(\frac{\partial \epsilon_{ij}}{\partial T} \right)_{\sigma, \epsilon} dT \\
d\mathcal{D}_i &= \left(\frac{\partial \mathcal{D}_i}{\partial \sigma_{jk}} \right)_{\epsilon, T} d\sigma_{jk} + \left(\frac{\partial \mathcal{D}_i}{\partial \mathcal{E}_j} \right)_{\sigma, T} d\mathcal{E}_j + \left(\frac{\partial \mathcal{D}_i}{\partial T} \right)_{\sigma, \epsilon} dT \\
dS &= \left(\frac{\partial S}{\partial \sigma_{ij}} \right)_{\epsilon, T} d\sigma_{ij} + \left(\frac{\partial S}{\partial \mathcal{E}_i} \right)_{\sigma, T} d\mathcal{E}_i + \left(\frac{\partial S}{\partial T} \right)_{\sigma, \epsilon} dT.
\end{aligned} \tag{5.11.2}$$

The above scheme actually involves $9 + 3 + 1 = 13$ distinct equations, each containing 13 independent variables. Proceeding across the various entries we find the following: (1,1): elasticity, all σ_{rs} except σ_{kl} remain fixed; (1,2): converse piezoelectricity; (1,3): thermal expansion; (2,1): direct piezoelectricity, all σ_{rs} except σ_{jk} remain fixed; (2,2): electrical permittivity; (2,3): pyroelectricity; (3,1): piezocaloric effect, all σ_{rs} except σ_{ij} remain fixed; (3,2): electrocaloric effect; (3,3): $C_{\sigma, \epsilon}/T$.

Based on this simple approach, one thus predicts the existence of a multitude of inter-dependent properties of anisotropic crystals subjected simultaneously to stress, electric fields, and temperature differences. These may be explored by construction of the thermodynamic functions of state that include $-\mathcal{D}_i d\mathcal{E}_i$ (summed over all components) in their differentials, as explained in conjunction with Eq. (5.7.1). The specialized energy in differential form per unit volume thus reads (cf. Eq. (5.7.2), with omission of the zero subscript, and replacement of \mathcal{P} by \mathcal{D})

$$d\mathcal{E}_{\sigma, \epsilon} = \sigma_{ij} d\epsilon_{ij} - \mathcal{E}_i d\mathcal{D}_i + T dS, \tag{5.11.3}$$

and the specialized Helmholtz free energy, defined as $A_{\sigma, \epsilon} = \mathcal{E}_{\sigma, \epsilon} - \sigma_{ij} \epsilon_{ij} - TS$, reads (cf. Eq. (5.7.3))

$$dA_{\sigma, \epsilon} = -\epsilon_{ij} d\sigma_{ij} - \mathcal{D}_i d\mathcal{E}_i - S dT. \tag{5.11.4}$$

The above may be compared with the differential form

$$dA_{\sigma, \epsilon} = (\partial A_{\sigma, \epsilon} / \partial \sigma_{ij})_{\epsilon, T} d\sigma_{ij} + (\partial A_{\sigma, \epsilon} / \partial \mathcal{E}_i)_{\sigma, T} d\mathcal{E}_i + (\partial A_{\sigma, \epsilon} / \partial T)_{\sigma, \epsilon} dT, \tag{5.11.5}$$

with the identifications (all σ_{rs} except σ_{ij} remain fixed)

$$(\partial A_{\sigma, \epsilon} / \partial \sigma_{ij})_{\epsilon, T} = -\epsilon_{ij}; \quad (\partial A_{\sigma, \epsilon} / \partial \mathcal{E}_i)_{\sigma, T} = -\mathcal{D}_i; \quad (\partial A_{\sigma, \epsilon} / \partial T)_{\sigma, \epsilon} = -S. \tag{5.11.6}$$

A double cross-differentiation then leads to the following results:

$$-\frac{\partial^2 A_{\sigma, \epsilon}}{\partial \sigma_{ij} \partial \mathcal{E}_k} = \left(\frac{\partial \epsilon_{ij}}{\partial \mathcal{E}_k} \right)_{\sigma, T} = \left(\frac{\partial \mathcal{D}_k}{\partial \sigma_{ij}} \right)_{\epsilon, T} \equiv d_{kij}^T \tag{5.11.7}$$

$$-\frac{\partial^2 A_{\sigma,\varepsilon}}{\partial \sigma_{ij} \partial T} = \left(\frac{\partial \varepsilon_{ij}}{\partial T} \right)_{\sigma,\varepsilon} = \left(\frac{\partial S}{\partial \sigma_{ij}} \right)_{\varepsilon,T} \equiv \alpha_{ij}^{\varepsilon} \quad (5.11.8)$$

$$-\frac{\partial^2 A_{\sigma,E}}{\partial \mathcal{E}_i \partial T} = \left(\frac{\partial \mathcal{D}_i}{\partial T} \right)_{\sigma,\varepsilon} = \left(\frac{\partial S}{\partial \mathcal{E}_i} \right)_{\sigma,T} \equiv p_i^{\sigma}. \quad (5.11.9)$$

These Maxwell relations show that the matrix elements in Eq. (5.11.2) are symmetric about the diagonals. Specifically, the coefficients of the direct and converse piezoelectric effects are equal—a conclusion that verifies an earlier statement in Section 5.10. Also, the coefficients for the thermal expansion and for the piezocaloric, as well as for the pyroelectric and electrocaloric effects, respectively, are identical. Again, bear in mind that Eq. (5.11.2) represents six relations for ε_i , three relations for \mathcal{D}_i , and one equation for dS each of which contains six variables σ_{ij} , three variables E_i , and T as the independent quantities.

In similar fashion, one may construct a generalized Gibbs free energy, with ε_{ij} , \mathcal{E}_i , T as independent variables, whose differential assumes the form

$$dG_{\sigma,\mathcal{D}} = \sigma_{ij} d\varepsilon_{ij} - \mathcal{D}_i d\mathcal{E}_i - S dT, \quad (5.11.10)$$

and whose double differentiation leads to the following Maxwell relations (all σ_{rs} except σ_{ij} or σ_{jk} remain fixed)

$$\left(\frac{\partial S}{\partial \mathcal{E}_i} \right)_{T,\varepsilon} = \left(\frac{\partial \mathcal{D}_i}{\partial T} \right)_{\varepsilon,\varepsilon}; \quad \left(\frac{\partial S}{\partial \varepsilon_{ij}} \right)_{T,\varepsilon} = - \left(\frac{\partial \sigma_{ij}}{\partial T} \right)_{\varepsilon,\varepsilon}; \quad \left(\frac{\partial \mathcal{D}_i}{\partial \varepsilon_{jk}} \right)_{\varepsilon,T} = - \left(\frac{\partial \sigma_{jk}}{\partial \mathcal{E}_i} \right)_{\varepsilon,T}. \quad (5.11.11)$$

It is left as an exercise to construct the seven remaining generalized thermodynamic functions whose double differentiation leads to a collage of all possible additional Maxwell relations. The construction of the linear phenomenological equations based on the choice of the independent variables of Eq. (5.11.10) is also left as an exercise.

Conditions that Fix the State of a System

For a complete specification of mechanical compliances, it is necessary carefully to specify the conditions under which a given measurement is carried out: thus, one must state not only whether it is S or T that is kept fixed, but also whether \mathcal{E}_i or \mathcal{D}_i and whether, σ or ε components are kept constant. When all $\mathcal{E}_i = 0$, the surfaces of the crystal must be at the same potential; the material is then said to be *electrically free*; when $\mathcal{D}_i = 0$, the crystal is said to be *electrically clamped*. The latter condition is not readily experimentally realized; for details, interested readers are referred to Nye, (Oxford, 1957) Constancy of σ components demands that the crystal be mounted so as to allow the strains to take place in as unhindered a fashion as possible; the material is then *mechanically free*. Constancy of ε components requires that, ideally, the crystal be firmly attached to a medium with infinite elastic stiffness; the material is then *mechanically clamped*.

Cross-interaction Effects

The above has set the stage for a more systematic exploration of the cross-interacting effects that can be studied. Let us consider one case in detail: Refer back to Eq. (5.11.2) and set $dT = 0$, with all σ_{rs} except σ_{pq} or σ_{kl} fixed:

$$\begin{aligned}
d\epsilon_{mn} &= \left(\frac{\partial \epsilon_{mn}}{\partial \sigma_{pq}} \right)_{\mathcal{E}} d\sigma_{pq} + \left(\frac{\partial \epsilon_{mn}}{\partial \mathcal{E}_j} \right)_{\sigma} d\mathcal{E}_j \\
d\mathcal{D}_i &= \left(\frac{\partial \mathcal{D}_i}{\partial \sigma_{kl}} \right)_{\mathcal{E}} d\sigma_{kl} + \left(\frac{\partial \mathcal{D}_i}{\partial \mathcal{E}_j} \right)_{\sigma} d\mathcal{E}_j.
\end{aligned} \tag{5.11.12}$$

Now set $d\epsilon_{mn} = 0$ and multiply the top equation by $(\partial \sigma_{kl} / \partial \epsilon_{mn})_E$. Then

$$0 = \left(\frac{\partial \sigma_{kl}}{\partial \epsilon_{mn}} \right)_{\mathcal{E}} \left(\frac{\partial \epsilon_{mn}}{\partial \sigma_{pq}} \right)_{\mathcal{E}} d\sigma_{pq} + \left(\frac{\partial \sigma_{kl}}{\partial \epsilon_{mn}} \right)_{\mathcal{E}} \left(\frac{\partial \epsilon_{mn}}{\partial \mathcal{E}_j} \right)_{\sigma} d\mathcal{E}_j. \tag{5.11.13}$$

On introducing the Kronecker deltas, the first term in Eq. (5.11.13) assumes the form $\delta_{kp}\delta_{lq}d\sigma_{pq} = d\sigma_{kl}$. Solve for $d\sigma_{pq}$ and substitute it in the second equation of Eq. (5.11.12) and divide by $d\mathcal{E}_j$. The result may be rewritten in the form

$$\left(\frac{\partial \mathcal{D}_i}{\partial \mathcal{E}_j} \right)_{\mathcal{E}} - \left(\frac{\partial \mathcal{D}_i}{\partial \mathcal{E}_j} \right)_{\sigma} = - \left(\frac{\partial \mathcal{D}_i}{\partial \sigma_{kl}} \right)_{\mathcal{E}} \left(\frac{\partial \sigma_{kl}}{\partial \epsilon_{mn}} \right)_{\mathcal{E}} \left(\frac{\partial \epsilon_{mn}}{\partial \mathcal{E}_j} \right)_{\sigma}. \tag{5.11.14}$$

The first and second terms on the left are entries κ_{ij} in the *permittivity tensor* that relates the electric displacement to the applied electric field under the indicated constraints. The first factor on the right corresponds to the quantity d_{ikl} introduced in Eqs. (5.10.19); the second factor, to the quantity c_{klmn} of Eq. (5.10.12); the third factor, to d_{jmn} as specified in Eq. (5.10.23). Accordingly, we find that at constant T , the difference between clamped and free permittivities is specified by

$$k_{ij}^{\mathcal{E}} - k_{ij}^{\sigma} = -d_{ikl}d_{jmn}c_{klmn}^{\mathcal{E}} \tag{5.11.15}$$

A similar approach is used to obtain many other interrelations of the type displayed in Eq. (515). These are shown in the Table 5.11.I which is compiled from Nye (Oxford, 1957).

Reference and Exercise

5.11.1. J.F. Nye, *Physical Properties of Crystals* (Clarendon Press, Oxford, 1957).

5.11.2. Set up the full set of Maxwell-type relations by first writing down expressions for all possible thermodynamic functions of state.

Table 5.11.1 Interrelations between Anisotropy Coefficients under Various Experimental Conditions

The dependent experimental variables are shown on the left and the independent variables are listed on top:

	σ	ε	T	
$\varepsilon $	s	d	α	
$\mathcal{D} $	d	κ	p	$\beta \equiv \kappa^{-1}$
$S $	α	p	C/T	

- (1) Thermoelastic compliances at constant electric fields:

$$s_{ijkl}^S - s_{ijkl}^T = -\alpha_{ij}\alpha_{kl}T/C^\sigma$$

- (2) Piezoelectric contribution to isothermal elastic compliances:

$$s_{ijkl}^{\mathcal{D}} - s_{ijkl}^{\mathcal{E}} = -d_{mij}d_{nkl}\beta_{mn}^\sigma$$

- (3) Electric field contribution to isothermal permittivities:

$$\kappa_{ij}^{\mathcal{E}} - \kappa_{ij}^\sigma = -d_{ikl}d_{jmn}c_{klmn}^{\mathcal{E}}$$

- (4) Pyroelectric contribution to permittivities at constant stress:

$$\kappa_{ij}^S - \kappa_{ij}^T = -p_i p_j T/C^\varepsilon$$

- (5) Pyroelectric contribution to the heat capacity at constant stress:

$$C^{\mathcal{D}} - C^{\mathcal{E}} = -Tp_i p_j \beta_{ij}^T$$

- (6) Thermoelastic contribution to the heat capacity at constant electric field:

$$C^{\mathcal{E}} - C^\sigma = -T\alpha_{ij}\alpha_{kl}c_{ijkl}^T$$

- (7) Isothermal elastic compliances: $(\partial\varepsilon_{ij}/\partial\sigma_{kl})_{D_1, E_2, E_3} \equiv s_{ijkl}^*$

$$s_{ijkl}^* - s_{ijkl}^{\mathcal{E}} = -d_{1ij}d_{1kl}/\kappa_{11}^\sigma$$

- (8) Pyroelectric-electrocaloric coefficients:

$$p_i^\varepsilon - p_i^\sigma = -\alpha_{jk}^{\mathcal{E}}c_{jklm}^{\mathcal{E}, T}d_{ilm}^T$$

- (9) Thermal expansion-piezocaloric effects:

$$\alpha_{ij}^{\mathcal{D}} - \alpha_{ij}^{\mathcal{E}} = -d_{kij}^T\beta_{kl}^{\sigma, T}p_l^\sigma$$

- (10) Direct and converse piezoelectric coefficients:

$$d_{ijk}^S - d_{ijk}^T = -p_i^\sigma\alpha_{jk}^{\mathcal{E}}T/C^{\sigma, \mathcal{E}}$$

5.12 Thermodynamics of Interacting Electron Assemblies

Introductory Comments

So far in discussing properties of electrically charged entities, we have largely concentrated on characteristics of ionic constituents. We now turn to a study of an assembly of interacting electrons in poorly conducting materials, based on a model developed by Spalek and coworkers.¹

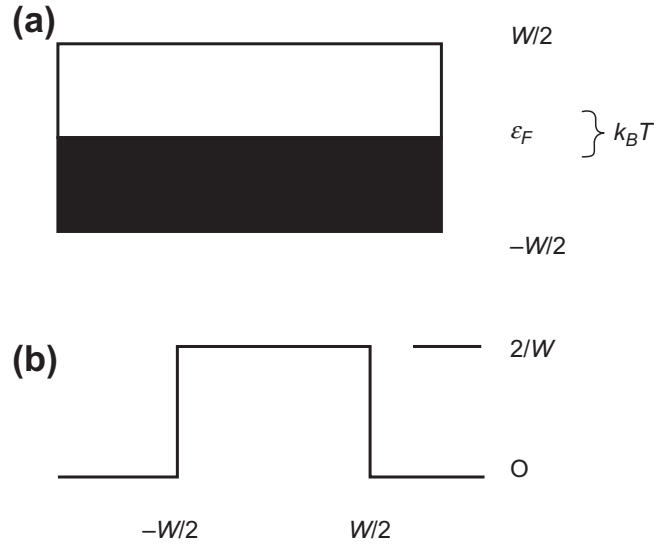


FIGURE 5.12.1

(a) Representation of a half-filled nondegenerate energy band; ε_F is the energy of the highest occupied state. (b) Rectangular density of states diagram; $\rho_d = 2/W$ in the energy range $-W/2 \leq \varepsilon \leq W/2$. The range of electronic thermal energies is indicated by the curly brackets.

Electron States in Bands

So long as the electronic interactions are moderate, the standard free-electron model for metals represents a good first-order approximation. However, there exist many materials in which the electron interactions are too strong to be modeled by this approach. For a study of electron itineracy under such conditions, we must modify the free-electron band structure model: even so, the free-electron theory serves as a point of departure. Quantum mechanics establishes that the energy states of N atoms in a metal consist of N tightly bunched energy levels that form so-called energy bands, which are separated by gaps, that is, energy states not allowed by quantum mechanics. We now introduce a number of simplifications; while not terribly realistic, they allow us to demonstrate the essentials of strongly interacting electrons. We consider only the highest lying occupied energy band, one that is only partially filled by electrons. A pictorial sketch for a half-filled band is shown in Figure 5.12.1(a): in the nondegenerate case shown here, the Pauli exclusion principle restricts the occupancy of every energy level in the band to at most two electrons with reversed spins. Let n represent the averaged number of outer electrons per lattice atom. The representative band is then fully occupied when $n = 2$. We set the zero of energy for an electron at an infinite distance away from the material (the ionization energy). We further restrict consideration to the rectangular density-of-states (RDOS) shown in Figure 5.12.1(b); electronic energies ε then lie in the range $-W/2 \leq \varepsilon \leq W/2$, and the density of states is specified by $\rho_d = 2/W$ within this range and zero outside. For the half-filled case at $T = 0$ K (for $n = 1$), all levels at and below $\varepsilon = -\varepsilon_F$ (the so-called

Fermi level) are completely filled, and the remainder are empty. If the electron occupancy exceeds $n = 1$, we revert to the hole formalism that we will not pursue here.

Note that in the free-electron case, the band width W normally is very much larger than the thermal energy $k_B T$ per electron, so that only electrons with energy ε close to ε_F have thermal access to empty states. Thus, only levels with energies in the range $\varepsilon_F \pm k_B T$ tend to be partially occupied; all others are either full or empty. By contrast, when constituent lattice atoms are separated by larger than normal distances, the larger separations correspond to much smaller bandwidths² W , in which case $k_B T$ becomes more nearly comparable to W , as sketched in the diagram. In this situation, electrons are subject to larger than normal electron interactions.

To take these factors into account, one must incorporate aspects of the electron hopping model. For this purpose, it has been proposed¹ to modify the kinetic energy ε_k of each free electron by introducing a universal scaling law $E_k = \Phi(\eta)\varepsilon_k$, $0 \leq \Phi(\eta) \leq 1$. The idea is to preserve the one-particle aspect of electron motion, by setting the free-electron kinetic energy at $\varepsilon_k = \hbar^2 k^2 / 2m$, where $\hbar k$ is the (quantized) linear momentum of the electron. The electron interactions are then simulated via the factor $\Phi(\eta)$ that mimics a hindrance to their movement, representing the difficulty that strongly interacting electrons have in moving past each other. Here η represents the probability of encountering a doubly occupied lattice site (or state), where the electron interactions are the strongest. In this simple model, interactions between electrons on nearest neighbor or more distant sites are ignored. Electrons engaging in such interactions for lack of a better term will be termed (somewhat inaccurately³) *quasi-particles*. As shown above, their energies are quantized via the energy quantization ε_k of their free-electron counterparts according to the associated momentum $\hbar k$. Normally, the spacing between adjacent quantum states is so small that at ordinary temperatures, ε may be considered as quasi-continuous, except where an enumeration of states is called for.

We first examine the effect of introducing the above scaling function. The band energy of the quasi-particle assembly is given by

$$E_B / N = \int_{-\infty}^{\infty} E \rho_d(E) f(E) dE. \quad (5.12.1)$$

Consider first $f(E)$, the energy distribution function appropriate to quasi-particles, which is obtained by adaptation of the Fermi–Dirac distribution, Eq. (10.1.9); n has been replaced by f . On adopting $E_k = \Phi(\eta)\varepsilon_k$, we see that

$$f(E_k) \equiv f[(E_k - E_F) / k_B T] \equiv f[(\varepsilon_k - \varepsilon_F) / k_B T^*] \equiv f^*(\varepsilon_k), \quad (5.12.2)$$

in which E_F is the Fermi energy, corresponding to $\varepsilon_F \equiv \mu$, in Figure 5.12.1(a), i.e. to the highest occupied energy level at $T = 0$; $\mu \equiv E_F / \Phi$ is an effective chemical potential and $T^* \equiv T / \Phi$ is an effective temperature. The above equation shows that the distribution function for the quasi-particles is equivalent to the Fermi–Dirac function for free particles at the higher effective temperature $T^* > T$: Thereby the thermal energy of the quasi-particles becomes more nearly comparable to the band width, as claimed earlier.

Next, we attend to the ρ_d factor in Eq. (5.12.1). The density of states (DOS) involves quantized energies ε_k that we enumerate by using the Dirac delta function $\delta(\varepsilon - \varepsilon_k)$ to sweep past all discrete ε_k

levels; this “function” vanishes unless $\varepsilon = \varepsilon_k$, where it has the value unity. We adapt this to the present case as shown below:

$$N\rho_d(E) = \sum_k \delta[\Phi \cdot (\varepsilon - \varepsilon_k)] = \sum_k \Phi^{-1} \delta(\varepsilon - \varepsilon_k) = \Phi^{-1}(\eta) \rho_{d0}(\varepsilon) N. \quad (5.12.3)$$

Here, we have introduced the relation $\delta(ax) = |a|^{-1} \delta(x)$ that applies to Dirac delta functions containing a constant factor a . Equation (5.12.3) shows that the DOS for correlated electrons, ρ_d , is increased by the factor $\Phi^{-1}(\eta) > 1$, relative to that of free electrons, ρ_{d0} . This points to a closer bunching of the N energy levels in the band than for free electrons, thus, to a narrowing of the band, as claimed earlier.

The upshot of all this reconfiguration is that the energy for quasi-particles in the band may be written as

$$E_k/N = \Phi(\eta) \int \varepsilon f^*(\varepsilon) \rho_0(\varepsilon) d\varepsilon \equiv \Phi(\eta) \bar{\varepsilon}(T^*). \quad (5.12.4)$$

We have thereby separated the band energy into a product of two factors, the second of which involves the average kinetic (transport) energy $\bar{\varepsilon}(T^*)$ for *bare electrons* at the effective temperature T^* , and the first of which attends to the electron interactions that give rise to band narrowing effects.

To the above, we need to add the interactions between electrons. Here we invoke the so-called *Hubbard interaction potential* U that specifies the potential energy when two electron with reversed spins reside on the same site with probability η . Again, we neglect the somewhat weaker (but in many cases, not negligible) interactions between electrons on adjacent or more distant sites. The total energy for the simple model under the consideration reads

$$E_B/N = \Phi(\eta) \bar{\varepsilon}(T^*) + U\eta. \quad (5.12.5)$$

Specification of Band Narrowing at $T = 0$

So far, so good, but all of the above is formal until we learn how to specify the function $\Phi(\eta)$. We must now distinguish between electron in “spin-up” (σ_\uparrow) and “spin-down” (σ_\downarrow) states. Here we note that $\eta \leq 1/4$ represents the upper limit that is reached when all electrons in the half-filled band are paired. It is thus apposite to expand Φ in powers of η as

$$\Phi = f_0 + f_1\eta + f_2\eta^2 + \dots \quad (5.12.6)$$

The expansion coefficients are determined by imposing boundary conditions that depend on electron transfers between adjacent sites. In the absence of externally applied fields, we expect that for the two-spin states, $n_\uparrow = n_\downarrow = n/2$.

(i) When $U = 0$, relative to the chosen zero of energy, and at $T = 0$, $\Phi = 1$; then

$$E_B/N|_{U=0} = \bar{\varepsilon} = -(W/2)n(1 - n/2). \quad (5.12.7a)$$

This is so because for an electron with a given spin to acquire kinetic energy, such an electron must have available a nearest neighbor site not already occupied by an electron of the same spin. The

probability of encountering such an electron is $n/2$ and the same for the appropriate empty configuration is $(1 - n/2)$. This gets multiplied by the total band energy. The associated probability of a random double occupancy is

$$\eta_0|_{U=0} = n^2/4. \quad (5.12.7b)$$

- (ii) Consider next the case where the Hubbard potential is infinite, so that no double occupancies are allowed; $\eta = 0$. Then the band (kinetic) energy at $T = 0$ is given by

$$E_B/N|_{\eta=0} = f_0\bar{\epsilon} = -(W/2)n(1 - n), \quad (5.12.8)$$

because an electron of either spin (probability $n/2$) cannot execute a jump unless an empty nearest-neighbor site is available.

On combining Eqs. (5.12.7) and (5.12.8), we find that

$$f_0 = (1 - n)/(1 - n/2). \quad (5.12.9)$$

- (iii) In the limit of no interactions, $U = 0$, the above must reduce to the free electron case, with $\eta = n^2/4$. Correspondingly, $V = 1$, and

$$f_0 + (n^2/4)f_1 + (n^4/16)f_2 = 1. \quad (5.12.10)$$

- (iv) We determine the equilibrium value for double occupancy by imposing the constraint $\partial(E_B/N)/\partial\eta = 0$; then

$$\eta_0 = -(1/2f_2)(f_1 + U/\bar{\epsilon}). \quad (5.12.11a)$$

But for $U = 0$, $\eta_0 = n^2/4$, whence,

$$-f_1/2f_2 = n^2/4. \quad (5.12.11b)$$

The above relations may be solved to yield

$$f_1 = \frac{4}{n(1 - n/2)}, \quad f_2 = \frac{-8}{n^3(1 - n/2)}, \quad (5.12.12)$$

in addition to Eq. (5.12.9).

We now restrict ourselves further to the special case of an exactly half-filled band, $n = 1$. In that event, $f_0 = 0$, $f_1 = 8$, and $f_2 = -16$. Moreover, at $T = 0$, and for an RDOS, $\bar{\epsilon} = -W/4$, so that the optimized double occupancy of band states, based on Eq. (5.12.11a), is given by

$$\eta_0 = \frac{1}{4} \left[1 - \frac{U}{2W} \right], \quad (5.12.13)$$

while

$$\Phi_0(\eta) = 8\eta_0(1 - 2\eta_0) = 1 - (U/2W)^2, \quad (5.12.14)$$

and the band energy is specified, via Eqs. (5.12.5), (5.12.13), and (5.12.14) as

$$\frac{E_B}{N} = -\frac{W}{4} \left[1 - \frac{U}{2W} \right]^2. \quad (5.12.15)$$

As anticipated, with growing U , the degree of double occupancy, the band energies, and the band narrowing factor Φ all diminish. A critical value is reached when $U = 2W$, where these quantities vanish. Beyond that point, they assume unphysical values—a transition to another state has taken place that we investigate below.

You should note once more the many drastic simplifying assumptions that have been introduced and that will be retained below. Nevertheless, the elimination of these restrictions will only change the numerics; the basic features here and below are not fundamentally altered.

Extension to Nonzero Temperatures

Up to this point, we have considered the transport properties at $T = 0$. When $T > 0$, the entropy contributions must be added to the energy of the quasi-electron assembly. The resulting free energy per itinerant quasi-particle is then specified as the energy plus the entropic contribution that includes both occupied and unoccupied states,

$$F_i/N = \sum_k \{E_k f(E_k) + U\eta + k_B T [f(E_k) \ln f(E_k) + (1 - f(E_k)) \ln(1 - f(E_k))]\}. \quad (5.12.16)$$

On now introducing Eq. (5.12.2) and $T = T^*\Phi$, we obtain the scaled version

$$F_i/N = \Phi(\eta) F_0(T^*)/N, \quad (5.12.17)$$

where F_0 refers to the noninteracting electron assembly at the effective temperature T^* , namely

$$F_0/N = \sum_k \{E_k f(\epsilon_k) + k_B T^* [f(\epsilon_k) \ln f(\epsilon_k) + (1 - f(\epsilon_k)) \ln(1 - f(\epsilon_k))]\}, \quad (5.12.18)$$

and where the electron interactions are subsumed via the factor $\Phi(\eta)$.

At relatively low temperatures, we are allowed to employ the Sommerfeld approximation to the heat capacity C_e of metals. Allowing for a factor of two for the two electron spin configurations, we write

$$C_e/N = \gamma(\epsilon_F) T; \quad \gamma \equiv 2\pi^2 k_B^2 \rho_e(E_F)/3 = 2\pi^2 k_B^2 \rho_0(E_F)/3\Phi = \gamma_0/\Phi, \quad (5.12.19)$$

where we have used Eq. (5.12.3) to switch from the DOS of quasi-particles to that of free electrons. Note the important point that as the interactions grow, Φ shrinks indefinitely, and the heat capacity of the heavy electron assembly rises correspondingly. This is one hallmark for the identification of electron interactions in metals, as was first pointed out by Brinkman and Rice.⁴

Phase Stability

We can now determine the low-temperature energy of each itinerant quasi-particle as

$$E_i(T)/N = -\Phi |\epsilon| + U\eta + \gamma_0 T^2/2\Phi, \quad (5.12.20)$$

and from the heat capacity, its entropy is given by

$$S_i(T)/N = \gamma_0 T / \Phi. \quad (5.12.21)$$

Then the free-energy functional reads

$$F_i(T)/N = -\Phi |\bar{\epsilon}| + U\eta - \gamma_0 T^2 / 2\Phi. \quad (5.12.22)$$

This is not yet the thermodynamic free energy because η has not been optimized. For this purpose, impose the constraint $(\partial F_i / \partial \eta) = 0$. It is intuitively evident that at sufficiently low temperatures the last term, involving the temperature, will be small relative to the first. Thus, in first-order approximation, no appreciable error is made in adopting Eqs. (5.12.13) and (5.12.14) as the appropriate optimizations. This conjecture is confirmed by carrying out the required mathematical operation—a tedious operation that you should execute on your own.⁵ The resulting optimized dimensionless Helmholtz free energy (in units of W) for a half-filled band ($n = 1$) involves Eqs. (5.12.14) and (5.12.15) and reads

$$\frac{F_i}{NW} = -\frac{1}{4} \left[1 - \left(\frac{U}{2W} \right)^2 \right] + \frac{U}{4W} \left[1 - \frac{U}{2W} \right] - \frac{1}{2W} \frac{\gamma_0 T^2}{1 - (U/2W)^2} \equiv E_{i0} - BT^2, \quad (5.12.23)$$

which explicitly involves the ratios $U/2W$ and γ_0/W . Note the T^2 dependence of the Helmholtz free energy for quasi-particles in the itinerant state.

The above is to be contrasted with the free energies of strictly localized particles with zero kinetic energy:

$$F_l/NW = -(k_B T / W) \ln 2, \quad (5.12.24)$$

corresponding to the entropy of each electron that is in one of the two possible spin states. In this case, the Helmholtz free energy varies linearly with T .

Construction of Electronic Phase Diagrams; Reentrant Metallic Behavior

We can now compare the stability of the itinerant vs the localized electronic state, and to determine whether transitions between them may occur. We first discuss this question at a qualitative level.

In Figure 5.12.2, we sketch a series of parabolas of F_i vs T^2 , Eq. (5.12.23), whose location on the diagram depends on the intercept E_0 . These parabolas for the itinerant state should be compared with the location of the straight line, corresponding to Eq. (5.12.24), for the localized state, which passes through the origin of coordinates. The stability then depends on which phase has the lower free energy. As an example, curve 1 shows that for large negative intercepts, E_0 , the parabola lies well below the straight line; the metallic phase is always stable. This corresponds to a large negative first term in the central part of Eq. (5.12.23), that far outweighs the positive repulsive term. Curve 2, by contrast, starts off with a small positive E_0 intercept. Now the straight line lies below the parabola up to the cross-over point R ($T = T_M$), beyond which the opposite situation holds. Thus, for $T < T_M$, the localized configuration is stable, which then gives way to the metallic state at higher temperatures. This is representative of the metal–insulator transitions that are encountered in many materials, such as transition metal oxides. Here the positive

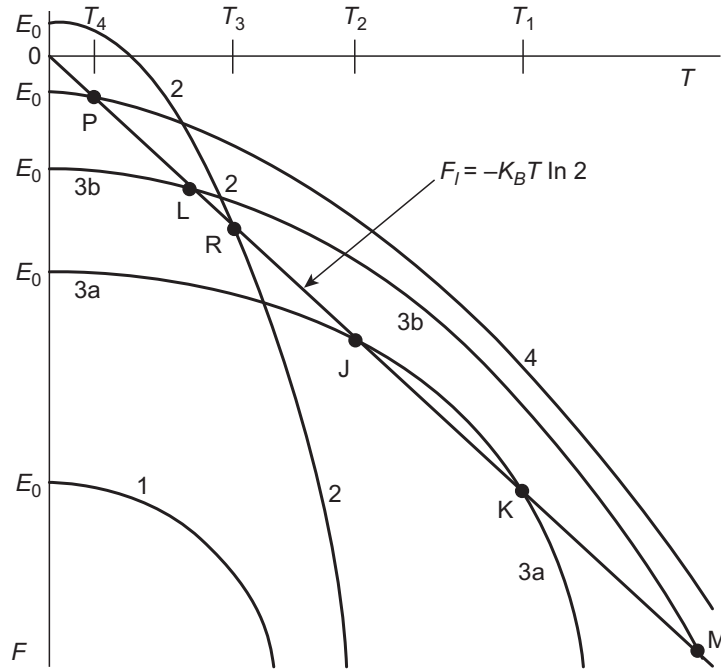


FIGURE 5.12.2

Sketch of the free energies F_i and F_l as a function of temperature, indicating transitions between localized and itinerant electronic states. For details, see text.

repulsive term in the central part of Eq. (5.12.23) initially slightly outweighs the itinerant contribution; the localization state is ultimately overcome by the onset of thermal effects at higher temperatures.

A very interesting situation arises in intermediate cases, as depicted in curves 3a and 3b, corresponding to a double intersection of the parabolas with the straight line. By the above arguments, curve 3b shows that the system is metallic up to point L on the diagram, then the insulating regime takes over and persists until point M is reached, after which the material reverts back to the metallic state. This is characteristic of *reentrant metallic behavior*, encountered in some special cases, such as Cr-doped V_2O_3 or $NiS_{2-x}Se_x$. It arises when the itinerant and localized contributions of Eq. (5.12.23) are nearly in balance. As E_0 becomes more negative, the regime of localized behavior (J to K) narrows, as shown in curve 3a. Ultimately, a situation is reached where the parabola just touches the straight line; this corresponds to a second-order transition at the critical point. Finally, curve 4 depicts the case where the metallic state at very low temperatures is followed by a transition to the insulating regime at point P; this rather counterintuitive transition is also seen in some composition ranges in $NiS_{2-x}Se_x$.

Overall, the above analysis provides a rationale how the temperature effects associated with very small thermal energies $k_B T$ can drastically shift electronic states whose energies are larger by at least a factor of 10^2 : in poor metals, the itinerant and localized free energies are nearly in balance; which state prevails is then determined by the much smaller thermal contribution.

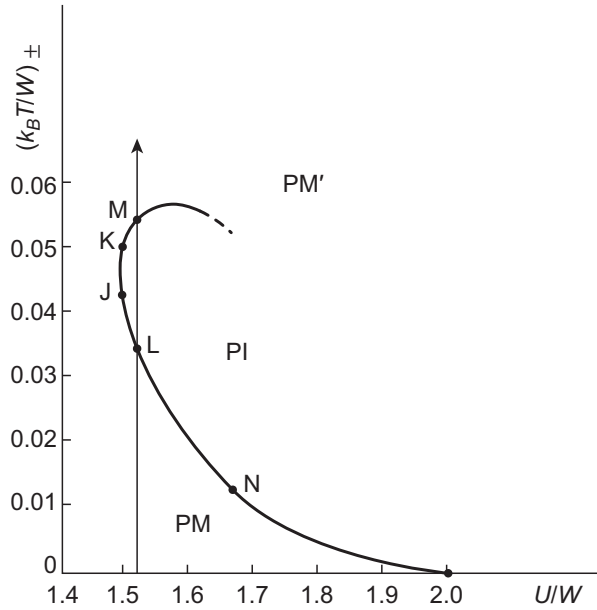


FIGURE 5.12.3

Phase diagram based on Eq. (5.12.25) for a rectangular DOS for $n = 1$. The retrograde curve indicates the phase boundary between the itinerant (PM, PM') and localized states. For details, see text.

We now quantify the above speculation. A transition between the two states occurs whenever the two reduced free energies, Eqs. (5.12.23) and (5.12.24) match. This leads to a quadratic equation in $k_B T / W$, with two roots:

$$\frac{k_B T}{W} = \frac{3}{2\pi^2} \left[1 - \left(\frac{U}{2W} \right)^2 \right] \left\{ \ln 2 \pm \left[(\ln 2)^2 - \frac{\pi^2 (1 - U/2W)^2}{3 (1 - (U/2W)^2)} \right]^{1/2} \right\}. \quad (5.12.25)$$

The resulting phase diagram is depicted in Figure 5.12.3 as a plot of $k_B T / W$ vs U/W . The retrograde curve represents the boundary line between the metallic phase and the insulating regime. Note that the curve has been artificially terminated both at $T = 0$ and at higher T , where the many approximations break down. Several features are of interest as follows: (i) There is a critical lower limit $(U/W)_l \approx 1.48$ and the coalescence value $(k_B T / W)_+ = (k_B T / W)_- \approx 0.045$, to the left of which only the metallic region is stable at all temperatures. (ii) At $T = 0$, only the metallic state prevails, even up to the terminal value $U = 2W$. (iii) Another critical point is located close to the cutoff point at $k_B T / W \approx 0.056$, $U/W \approx 1.56$. (iv) For fixed U/W in the limited range $1.48 \leq U/W \leq 1.56$, one encounters with rising T the reentrant metallic behavior, signaled by the sequence PM–PI–PM', as indicated by the representative vertical line in the figure. (v) In the range $1.56 \leq U/W \leq 2$, only the PM–PI transition is encountered with rising T .

Again, more sophisticated models, some based on a two-fluid model, can be constructed and analyzed. While the numerical values of the above parameters are now different, the basic structure of the theory remains intact.

Remarks and References

- 5.12.1.** J. Spalek, A.M. Oleś, J.M. Honig, *Phys. Rev. B* **28**, 6802 (1983); J. Spalek, *J. Solid State Chem.* **88**, 70 (1990).
- 5.12.2.** The bandwidth W is dictated by the separation distance between adjacent lattice atoms. The larger this distance the smaller is W , a situation common in transition metal oxides. The effect is mimicked by Eq. (9.5.12c). The screening constant κ , Eq. (9.5.5d) diminishes with concentrations c . This extends the range of the interaction potential ψ , which in the free-electron case is limited to atomic dimensions, but becomes much longer ranged in the case considered here.
- 5.12.3.** Actually that term is normally reserved for entities such as photons whose number is not conserved; but in the interest of simplicity, we shall use this appellation here.
- 5.12.4.** W.F. Brinkman and T.M. Rice, *Phys. Rev. B* **2**, 4302 (1971).
- 5.12.5.** Carry out the required optimization and convince yourself that adoption of the $T = 0$ optimization is appropriate.
- 5.12.6.** H. Kuwamoto, J. Appel, J.M. Honig, *Phys. Rev. B* **22**, 2626 (1980).
- 5.12.7.** X. Yao, J. Spalek, J.M. Honig, T. Hogan, C. Kannewurf, *Phys. Rev. B* **54**, 17469 (1996).

6.0 Introductory Comments

We now study thermodynamics in the proper sense of the word. We consider irreversible processes that arise because one or more intensive variables in a system are rendered nonuniform. So long as variations in T , P , and ρ (temperature, pressure, and density) or other intensive quantities are “small” relative to their average values, one can still apply the machinery of equilibrium thermodynamics as shown below. In what follows the identification of conjugate forces and fluxes, the Onsager reciprocity conditions (ORC), and the rate of entropy production play a central role.

6.1 Generalities

Nonequilibrium phenomena necessarily involve states in which different portions of a given system display different physical characteristics. To handle this situation, we subdivide the system into tiny subunits and allow all variables of interest to become functions of their position within the sample, as well as become functions of time. Thus, each thermodynamic variable ϕ_i of interest must be specified in terms of its position \mathbf{r} at time t : $\phi_i = \phi_i(\mathbf{r}, t)$.

We render such systems subject to the scrutiny of thermodynamics by establishing the *Principle of Local State* that is based on two assertions. (i) The instantaneous values of all thermodynamic quantities ϕ_i centered on a small region about the location \mathbf{r} satisfy the same general thermodynamic relationships as do the corresponding quantities for a large *uniform* copy of the same small region at that instant of time. (ii) The local, instantaneous gradients of ϕ_i , and their rates of change, are to be ignored within the volume element, when setting up the specification of the thermodynamic configurations. However, these quantities change as one proceeds to contiguous locations, thereby establishing gradations in properties as one proceeds to neighboring locations. As long as the variation in ϕ is “sufficiently small” within each small region under study (what “sufficiently small” means can generally only be decided by experiment), it may be left out of account.

When the quantities ϕ_i vary with time, one must specify a corresponding velocity function $\mathbf{v}(\mathbf{r}, t)$ to describe the change in properties of ϕ_i . However, if it so happens that the entities ϕ_i remain unaltered and that only the surroundings change, then the system has reached a *steady state* with respect to changes in these particular properties. A precise specification of this state is furnished in Section 6.4.

The General Balance Equations

Let $\phi(r, t)$ represent the quantity per unit mass whose distribution over the volume element is governed by the density function $\rho(r, t)$. The time-varying extensive variable for the entire system is then specified by

$$\varphi(t) = \int_{V(t)} \rho(r, t) \phi(r, t) d^3\mathbf{r}, \quad (6.1.1)$$

where, in general, the volume may depend on time. To take account of the variable limit of integration, reference is made to Figure 6.1.1: the system whose initial boundary is indicated by the solid curve passes in time dt to a volume indicated by the dotted curve. In general, this involves a deformation characterized by a center-of-mass change with velocity \mathbf{v} . In an infinitesimal lapse of time dt , the change $\partial\phi(t)/\partial t$ involves three contributions to the volume change of the system. (a) The first consists of the central region V' consisting of the two overlapping volumes, drawn as a shaded region in that figure; this contributes the quantity $dt \int_{V'} (\partial\rho\phi/\partial t) d^3\mathbf{r}$ to $\dot{\phi}dt$. In the limit $dt \rightarrow 0$, and keeping only first-order terms, one may ignore the difference between V and V' . (b) Next, there is a contribution from the sliver of volume V'' generated through the deformation process, as the region moves to the right. This sliver is composed of the elements $-\rho\phi(\mathbf{v} \cdot \hat{\mathbf{n}})d^2\mathbf{r}dt$, where $\hat{\mathbf{n}}$ is the outer unit vector normal to the surface element $d^2\mathbf{r}$ at the original boundary (hence, the minus sign; the original region “ingests” the new territory), and where the velocity \mathbf{v} points in the direction of motion of the small number of ϕ units of material crossing from V' into V'' . The overall contribution to $\dot{\phi}dt$ is therefore $-dt \int_{A''} \rho\phi(\mathbf{v} \cdot \hat{\mathbf{n}})d^2\mathbf{r}$. (c) A similar contribution, $-dt \int_{A'''} \rho\phi(\mathbf{v} \cdot \hat{\mathbf{n}})d^2\mathbf{r}$, arises from the elimination of the tiny volume V''' relinquished in the transfer. Contributions (b) and (c) are combined into a single integral $-dt \int_A \rho\phi(\mathbf{v} \cdot \hat{\mathbf{n}})d^2\mathbf{r}$, where the area A may be taken to extend over the original boundary.

It follows that the overall time rate of change in ϕ is specified by

$$\dot{\phi} = - \int_{A(t)} \rho\phi(\mathbf{v} \cdot \hat{\mathbf{n}})d^2\mathbf{r} + \int_{V(t)} [\partial(\rho\phi)/\partial t]d^3\mathbf{r}, \quad (6.1.2a)$$

where the second term attends to the local generation of ϕ . When Gauss' theorem is introduced, Table 1.3.I, line (k), we obtain

$$\dot{\phi} \equiv \int_{V(t)} [\partial(\rho\phi)/\partial t]d^3\mathbf{r} = \int_{V(t)} \{-\nabla \cdot (\rho\phi\mathbf{v}) + \partial(\rho\phi)/\partial t\}d^3\mathbf{r}, \quad (6.1.2b)$$

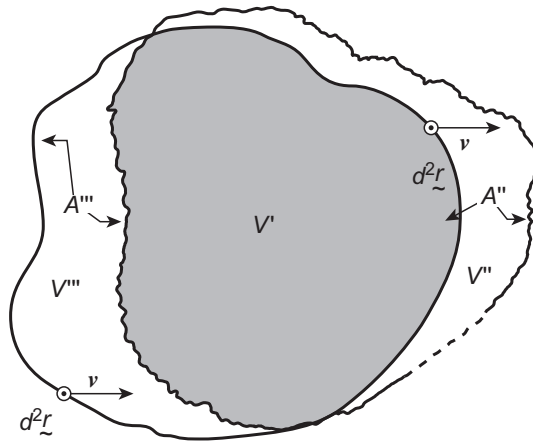


FIGURE 6.1.1

Change in volume of a system subjected to barycentric flow. A'' and A''' are the original and new boundaries during the change that generates volume V''' and eliminates volume V'' .

where on the right, we have reintroduced $\rho\phi$ as the density of ϕ . Equation (6.1.2b) must hold for every volume element, regardless of the time variation of the total volume. This can be generalized: consider a quantity R that is distributed at density $\rho_R(\mathbf{r})$ over a system with volume V ; $R = \int_V \rho_R(\mathbf{r}) d^3\mathbf{r}$. Also, let the rate of transport of R be designated by the *flux vector* $\mathbf{J}_R = \rho_R \mathbf{v}$. Then Eq. (6.1.2b) in elemental form is rewritten as a *balance equation*:

$$(\partial\rho_R/\partial t) = -\nabla\cdot\mathbf{J}_R + \dot{\rho}_R. \quad (6.1.3)$$

This expression is known as the *equation of continuity*. It clearly differentiates between processes that involve transport of R across boundaries and the local generation of R . However, in some situations, R as in the case of energy, cannot be generated locally; in that event, Eq. (6.1.3) specializes to

$$(\partial\rho_R/\partial t) = -\nabla\cdot\mathbf{J}_R, \quad (6.1.4)$$

known as a *conservation equation*; here, R can only be changed through transport across the boundaries of the system.

Now reintroduce the fundamental flux vector $\mathbf{J}_R = \rho_R \mathbf{v}$, so that, ignoring local R production,

$$\partial\rho/\partial t = -\nabla\cdot(\rho\mathbf{v}) = -\rho\nabla\cdot\mathbf{v} - \mathbf{v}\cdot\nabla\rho. \quad (6.1.5)$$

A trivial rearrangement leads to the result

$$\partial\rho/\partial t + \mathbf{v}\cdot\nabla\rho \equiv D\rho/Dt = -\rho\nabla\cdot\mathbf{v}, \quad (6.1.6)$$

where $D\rho/Dt$ is the *convected derivative*, i.e., the derivative with respect to time inside a volume element that moves with velocity \mathbf{v} relative to the center of mass of the system. A proof of this statement is furnished in the Appendix to this section. In many treatises, this particular quantity is written out as $d\rho/dt$.

We next consider several special cases that apply to Eq. (6.1.3).

Balance Equation for Concentration

Here we study processes that affect the (molar) concentration c_k of a chemical species k ; for this purpose, we set up a flux vector $c_k \mathbf{v}_k(\mathbf{r}, t)$ for the rate of transport of k at concentration c_k past location \mathbf{r} at time t . The total amount of k may be altered either through chemical reactions that change its concentration locally at a rate $(\partial c_k/\partial t)|_c$, or by convective or diffusive transport processes that take place at a rate $(\partial c_k/\partial t)|_t$. Convection relates to the motion of the center of mass of the system that carries all constituents with it, while diffusion relates to the motion of species k relative to the center of mass.

The velocity of the center of mass of the system of intermingling species k is given by

$$\mathbf{v} = \frac{\sum_k \mathbf{v}_k M_k c_k}{\sum_k M_k c_k} = \frac{\sum_k \mathbf{v}_k \rho_k}{\sum_k \rho_k}, \quad (6.1.7)$$

where M_k is the gram molecular mass of species k .

In the above, \mathbf{v}_k is the velocity of motion of species k . To determine the rate of entry of this species into a small volume element that itself moves with velocity \mathbf{v} , we now introduce the (*molar*)

flux vector relative to the center of mass for species k across perpendicular unit cross-section per unit time as

$$\mathbf{J}_R = c_k(\mathbf{v}_k - \mathbf{v}). \quad (6.1.8)$$

The time rate of change of material of type k in a local volume element other than through diffusion or convection occurs when this species participates in r distinct chemical reactions. We therefore write

$$\dot{\rho}_V = \sum_{l=1}^r \sum_{k=1}^n c_k \nu_{kl} \omega_l, \quad (6.1.9)$$

where, as before, the ν_{kl} are the stoichiometry coefficients (positive or negative) for all n species k participating (as products or reagents) in each of the r distinct chemical reactions, and $\omega_l \equiv d\lambda_l/dt$ is the rate of advancement of the l th chemical reaction.

Putting these results together, we write a balance equation for species k , based on Eqs. (6.1.3) and (6.1.8), as

$$\left(\frac{\partial c_k}{\partial t} \right) = \left(\frac{\partial c_k}{\partial t} \right) \Big|_t + \left(\frac{\partial c_k}{\partial t} \right) \Big|_c = -\nabla \cdot \mathbf{J}_k + \nabla \cdot (c_k \mathbf{v}) + \sum_{l=1}^r c_k \nu_{kl} \omega_l, \quad (6.1.10)$$

with the obvious identifications

$$\left(\frac{\partial c_k}{\partial t} \right) \Big|_t = -\nabla \cdot \mathbf{J}_k + \nabla \cdot (c_k \mathbf{v}); \quad \left(\frac{\partial c_k}{\partial t} \right) \Big|_c = \sum_{l=1}^r c_k \nu_{kl} \omega_l. \quad (6.1.11)$$

In the event that there is no convection in the system ($\mathbf{v} = 0$), we find

$$\left(\frac{\partial c_k}{\partial t} \right) = -\nabla \cdot \mathbf{J}_k + \sum_{l=1}^r c_k \nu_{kl} \omega_l \quad (6.1.12)$$

to be the basic *equation of conservation of mass* for species k .

Energy Balance Equation

The total energy density of a system involves contributions from the internal energy density e , the kinetic energy density \mathcal{K} , and the potential energy density \mathcal{V} . We consider first $\mathcal{K} = \frac{1}{2} \sum_k M_k c_k v_k^2$. It is a trivial matter verifying the identity

$$\begin{aligned} \frac{1}{2} \sum_k M_k c_k (\mathbf{v}_k - \mathbf{v})^2 &= \frac{1}{2} \sum_k M_k c_k v_k^2 - \sum_k M_k c_k \mathbf{v}_k \cdot \mathbf{v} + \frac{1}{2} \sum_k M_k c_k v^2 \\ &= \frac{1}{2} \sum_k M_k c_k v_k^2 - \mathbf{v} \cdot \sum_k \rho_k \mathbf{v}_k + \frac{1}{2} \sum_k \rho_k v^2 = -\frac{1}{2} \rho v^2 + \frac{1}{2} \sum_k M_k c_k v_k^2, \end{aligned} \quad (6.1.13)$$

where $\rho = \sum_k \rho_k$ is the total density of the system, and where Eq. (6.1.7) has been introduced. Inserting Eq. (6.1.13) into the kinetic energy density, $\mathcal{K} = \frac{1}{2} \sum_k M_k c_k v_k^2$, leads to the result

$$\mathcal{K} = \frac{1}{2} \rho v^2 + \frac{1}{2} \sum_k M_k c_k (\mathbf{v}_k - \mathbf{v})^2, \quad (6.1.14)$$

which breaks \mathcal{K} up into a term involving the motion of the center of mass, and the kinetic energies of the various species relative to the center of mass.

Henceforth, *we neglect the motion of the center of mass* (setting $\mathbf{v} = 0$) and now consider the time derivative of the internal energy density, as given by

$$\frac{\partial e(T, c_k)}{\partial t} = \hat{C}_V \frac{\partial T}{\partial t} + \sum_k \bar{e}_k \frac{\partial c_k}{\partial t} = \hat{C}_V \frac{\partial T}{\partial t} + \sum_k \sum_l \bar{e}_k c_k \nu_{kl} \omega_l - \sum_k \bar{e}_k \nabla \cdot \mathbf{J}_k, \quad (6.1.15)$$

in which \hat{C}_V is the heat capacity density at constant volume, and $\bar{e}_k \equiv (\partial e / \partial c_k)_{T, P, c_{k \neq i}}$ represents the partial molal energy density of species k . Here, Eq. (6.1.12) had been introduced to obtain the expression on the right; the middle term represents the “heat of reactions” dissipated or absorbed as the various chemical species participate in all of the chemical reactions in the system.²

It remains to consider the passage of material in externally applied fields (potentials) ψ , including external pressure, that are presumed to be time-invariant. We begin with Eq. (6.1.10), set $\mathbf{v} = 0$, and operate on both sides with $\sum_k \psi_k$, whence the potential energy density variation with respect to time is given by

$$\begin{aligned} \partial \mathcal{V} / \partial t &\equiv \sum_k \partial (\psi_k c_k) / \partial t = - \sum_k \psi_k \nabla \cdot \mathbf{J}_k + \sum_k \sum_l \psi_k c_k \nu_{kl} \omega_l \\ &= - \sum_k \nabla \cdot (\psi_k \mathbf{J}_k) + \sum_k \mathbf{J}_k \cdot \nabla \psi_k. \end{aligned} \quad (6.1.16)$$

The double sum in the middle vanishes because the potential energy of all constituents remains unaltered during the various chemical reactions within the system. Also, we used line (d) of Table 1.3.I in arriving on the right-hand side.

Putting Eqs. (6.1.14), (6.1.15) and (6.1.16) together, we now find an energy balance equation of the form

$$\begin{aligned} \frac{\partial u}{\partial t} &= \hat{C}_V \frac{\partial T}{\partial t} + \sum_k \sum_l \bar{e}_k c_k \nu_{kl} \omega_l - \sum_k \bar{e}_k \nabla \cdot \mathbf{J}_k - \nabla \cdot \sum_k \psi_k \mathbf{J}_k \\ &\quad + \sum_k \mathbf{J}_k \cdot \nabla \psi_k + d\mathcal{K} / dt. \end{aligned} \quad (6.1.17a)$$

In accordance with the first law, the total energy of a system can only be changed by energy transport across its boundaries. We therefore introduce a *total energy flux vector* \mathbf{J}_U by the conservation law

$$\partial u / \partial t = - \nabla \cdot \mathbf{J}_U \quad (6.1.17b)$$

In looking ahead to the theoretical development in later sections, it is expedient to separate out from the right-hand side of Eq. (6.1.17a) the last three terms, and to sum the remaining contributions as a time rate of change of the internal energy density, e . Thus, we combine the first three terms as follows:

$$\frac{\partial e}{\partial t} = \hat{C}_V \frac{\partial T}{\partial t} + \sum_k \sum_l \bar{e}_k c_k \nu_{kl} \omega_l - \sum_k \bar{e}_k \nabla \cdot \mathbf{J}_k, \quad (6.1.18)$$

so that

$$\frac{\partial u}{\partial t} = \frac{\partial e}{\partial t} - \nabla \cdot \sum_k \psi_k \mathbf{J}_k + \sum_k \mathbf{J}_k \cdot \nabla \psi_k + d\mathcal{K}/dt = -\nabla \cdot \mathbf{J}_U, \quad (6.1.19)$$

where we inserted from Eq. (6.1.17b) on the right. To render Eq. (6.1.19) compatible with Eq. (6.1.4), the first, third, and fourth terms in the middle must be regarded as equivalent to and expressible as minus the divergence of a flux vector that we shall call \mathbf{J}_Q . Thus, we set

$$\begin{aligned} -\nabla \cdot \mathbf{J}_Q &\equiv \frac{\partial e}{\partial t} + \sum_k \mathbf{J}_k \cdot \nabla \psi_k + d\mathcal{K}/dt = \hat{C}_V \frac{\partial T}{\partial t} + \sum_k \sum_l \bar{e}_k c_k v_{kl} \omega_l \\ &\quad - \sum_k \bar{e}_k \nabla \cdot \mathbf{J}_k + \sum_k \mathbf{J}_k \cdot \nabla \psi_k + d\mathcal{K}/dt. \end{aligned} \quad (6.1.20a)$$

We must digress briefly at this point. Let us write $\sum_k \mathbf{J}_k \cdot \nabla \psi_k = \sum_k \nabla \cdot \psi_k \mathbf{J}_k - \sum_k \psi_k \nabla \cdot \mathbf{J}_k$. Then it is seen that the negative divergence of the flux vector \mathbf{J}_Q must match not only the contributions $\sum_k \bar{e}_k \nabla \cdot \mathbf{J}_k$, $\sum_k \nabla \cdot \psi_k \mathbf{J}_k$, and $\sum_k \psi_k \nabla \cdot \mathbf{J}_k$, but also the remaining terms that do not have the form of a divergence function. This physically means that energy in terms of heat transfer must be supplied to or withdrawn from the system to keep pace with the *rate of energy changes* $\hat{C}_V(\partial T/\partial t)$, $\sum_k \sum_l \bar{e}_k c_k v_{kl} \omega_l$, and $d\mathcal{K}/dt$ that are specified in Eq. (6.1.20a), i.e., with the rate of change in temperature, the rate of change of energy internally through the occurrence of chemical reactions within the system, and the rate of change of the kinetic energy of the system. These effects cause a change in the internal energy of the system that in steady-state conditions must be matched, as already stated, by the flow of heat across the boundaries of the local system. In particular, it is important to distinguish the *rate of energy change* arising from chemical reactions, in which the various species k have different internal energies \bar{e}_k , from the effects of internal chemical reactions discussed in Section 1.16, that were altered by transport of chemical species across the boundaries.

For future use, we rewrite Eq. (6.1.20a) as

$$\partial e/\partial t = -\nabla \cdot \mathbf{J}_Q - \sum_k \mathbf{J}_k \cdot \nabla \psi_k - d\mathcal{K}/dt. \quad (6.1.20b)$$

Then, the energy density balance equation (6.1.19) reads

$$\partial u/\partial t = -\nabla \cdot \mathbf{J}_Q - \nabla \cdot \sum_k \psi_k \mathbf{J}_k = -\nabla \cdot \mathbf{J}_U. \quad (6.1.21a)$$

We therefore interrelate the various flux vectors as

$$\mathbf{J}_U = \mathbf{J}_Q + \sum_k \psi_k \mathbf{J}_k. \quad (6.1.21b)$$

We may term \mathbf{J}_Q as a *heat flux vector*; for, we have consistently viewed the net total energy change as arising from the flow of heat and from the performance of work. The latter involves the term $\sum_k \psi_k \mathbf{J}_k$. Note that \mathbf{J}_Q includes all the contributions shown in Eq. (6.1.20a).

Entropy Balance Equation and Rate of Local Entropy Production

For a system at constant volume, the second law is handled via the relation $Tds = de - \sum_k \mu_k dc_k$, for the entropy density, where μ_k is the chemical potential of species k . Accordingly,

$$T \frac{\partial s}{\partial t} = \frac{\partial e}{\partial t} - \sum_k \mu_k \frac{\partial c_k}{\partial t}. \quad (6.1.22)$$

We now introduce Eqs. (6.1.12) and (6.1.20b); we additionally *assume that the kinetic energy contribution remains time-invariant* (this quantity may also vanish). We then find

$$\partial s / \partial t = T^{-1} \left[-\nabla \cdot \mathbf{J}_Q + \sum_k \mathbf{J}_k \cdot \mathbf{f}_k - \sum_k \mu_k \nabla \cdot \mathbf{J}_k + \sum_l \mathcal{A}_l \omega_l \right], \quad (6.1.23)$$

in which $\mathcal{A}_l \equiv -\sum_k \mu_k c_k v_{kl}$ is known as the *chemical affinity*; we have also introduced the force density as $\mathbf{f}_k = -\nabla \psi_k$.

The next step consists in an extensive rewriting of the above equation; standard mathematical manipulations acting on Eq. (6.1.23) lead directly to the following equivalent form that you should take the trouble to verify:

$$\begin{aligned} \partial s / \partial t = & -\nabla \cdot \left[T^{-1} \left(\mathbf{J}_Q - \sum_k \mu_k \mathbf{J}_k \right) \right] - (1/T^2) \mathbf{J}_Q \cdot \nabla T + (1/T^2) \sum_k \mu_k \mathbf{J}_k \cdot \nabla T \\ & - (1/T) \sum_k \mathbf{J}_k (\nabla \mu_k - \mathbf{f}_k) + (1/T) \sum_l \mathcal{A}_l \omega_l. \end{aligned} \quad (6.1.24)$$

While this expression looks much more complicated, it is actually readily interpreted. Note that the quantity involving square brackets in the first term on the right-hand side represents the divergence of a set of flux vectors. Now, Eq. (6.1.3), specialized to the entropy balance, has the form

$$\partial s / \partial t = -\nabla \cdot \mathbf{J}_S + \dot{\theta}, \quad (6.1.25)$$

where \mathbf{J}_S is the entropy flux vector and $\dot{\theta}$ attends to the rate of locally generated entropy. Thus, it clearly makes sense to correlate the *entropy flux vector* \mathbf{J}_S with the term in square brackets in Eq. (6.1.24); we therefore set

$$\mathbf{J}_S = T^{-1} \left(\mathbf{J}_Q - \sum_k \mu_k \mathbf{J}_k \right). \quad (6.1.26)$$

The remaining terms on the right-hand side of Eq. (6.1.24) must then represent source terms $\dot{\theta}$; accordingly,

$$\dot{\theta} = -(1/T) \mathbf{J}_S \cdot \nabla T - (1/T) \sum_k \mathbf{J}_k \cdot \nabla \xi_k + (1/T) \sum_l \mathcal{A}_l \omega_l \geq 0. \quad (6.1.27)$$

in which we have now set $\nabla \mu_k - \mathbf{f}_k = \nabla(\mu_k + \psi_k) \equiv \nabla \xi_k$. Thus, ξ_k may be regarded as a *generalized chemical potential* for species k . Then, in Eq. (6.1.25), the term $-\nabla \cdot \mathbf{J}_S$ represents the net increase of entropy density across the boundaries of a volume element, whereas Eq. (6.1.27) refers to the generation of entropy density through irreversible processes occurring locally within the volume element. In subsequent discussions, Eq. (6.1.27) will play a cardinal role.

The specification of θ is not unique. We provide an alternate relation by combining Eq. (6.1.21b) with Eq. (6.1.26) to write³

$$\mathbf{J}_U = T\mathbf{J}_S + \sum_k \xi_k \mathbf{J}_k. \quad (6.1.28)$$

Now substitute this relation into Eq. (6.1.27); a slight rearrangement leads to the result

$$\begin{aligned} \dot{\theta} &= -(1/T)\mathbf{J}_U \cdot \nabla T - (1/T^2) \sum_k \mathbf{J}_k \cdot \nabla T - (1/T) \sum_k \mathbf{J}_k \cdot \nabla \xi_k + (1/T) \sum_l \mathcal{A}_l \omega_l \\ &= \mathbf{J}_U \cdot \nabla(1/T) - \sum_k \mathbf{J}_k \cdot \nabla(\xi_k/T) + (1/T) \sum_l \mathcal{A}_l \omega_l \geq 0. \end{aligned} \quad (6.1.29)$$

The form of Eqs. (6.1.27) and (6.1.29) is highly significant. In both cases, the rate of entropy density generation through irreversible processes taking place locally is specified by a sum of products of the general form $\dot{\theta} = \sum_\alpha \mathbf{J}_\alpha \cdot \mathbf{X}_\alpha \geq 0$ wherein the \mathbf{J}_α represent either *generalized fluxes* or *reaction velocities*, and the \mathbf{X}_α represent *generalized forces*. As explained in Section 2.2, this nomenclature is appropriate because $\dot{\theta} = 0$ only occurs when both the forces and the fluxes vanish. In this sense, the flux \mathbf{J}_α is a response to the imposition of an applied force \mathbf{X}_α . Of great importance in our future development are the particular forces and fluxes that occur pairwise in the expression $\dot{\theta} = \sum_\alpha \mathbf{J}_\alpha \cdot \mathbf{X}_\alpha$. The partners in these pairs are said to form *conjugate variables*: in Eq. (6.1.27), they are, respectively, $(\mathbf{J}_S/T, -\nabla T)$, $(\mathbf{J}_k/T, -\nabla \xi_k)$, $(\omega_l, \mathcal{A}_l/T)$; in Eq. (6.1.29), they are specified, respectively, by the set $(\mathbf{J}_U, \nabla(1/T))$, $(\mathbf{J}_k, -\nabla(\xi_k/T))$, $(\omega_l, \mathcal{A}_l/T)$. Which of the two sets of conjugate force–flux pairs are to be used in future derivations is simply a matter of convenience. No flux can occur without being “driven” by a force field; in its absence, $\dot{\theta}$ vanishes and Eq. (6.1.25) then becomes a conservation equation for entropy.

For many applications (Section 6.8), it is expedient to split the gradient $\nabla \xi_k$ into a component that involves T and a remainder involving mole fractions x , both of which are functions of positions r within the sample: $\xi_k = \xi_k(T, r) = \mu[T(r), x(r) + \psi(r)] = \xi_k[T(r), x(r)]$, so that

$$\begin{aligned} (\partial \xi / \partial r) &= (\partial \mu / \partial T)_x (\partial T / \partial r) + (\partial \mu / \partial x)_T (\partial x / \partial r) + (\partial \psi / \partial r) \\ &= -\bar{S} (\partial T / \partial r) + (\partial \mu / \partial x)_T (\partial x / \partial r) + \partial \psi / \partial r, \end{aligned} \quad (6.1.30a)$$

or, in abbreviated vector notation:

$$\nabla \xi = -\bar{S} \nabla T + \nabla \xi|_T, \quad (6.1.30b)$$

where the T subscript indicates that the partial derivative is to be taken at constant temperature. On introducing Eq. (6.1.30b) into Eq. (6.1.27), we combine the two ∇T contributions to find

$$\dot{\theta} = -(1/T) \mathbf{J}_S \cdot \nabla T - (1/T) \sum_k \mathbf{J}_k \cdot \nabla \xi_k|_T + (1/T) \sum_l \mathcal{A}_l \omega_l \geq 0, \quad (6.1.31)$$

wherein

$$\mathbf{J}_S \equiv \mathbf{J}_S - \sum_k \bar{S}_k \mathbf{J}_k \quad (6.1.32)$$

is the entropy flux arising from sources other than matter flow. The conjugate force–flux pairs now differ from those of Eq. (6.1.27).

Appendix

We elaborate here on Eq. (6.1.6): consider a function F that pertains to a volume element dV which at time t is at position \mathbf{r} and which moves with velocity \mathbf{v} to a new position $\mathbf{r} + \Delta\mathbf{r}$ at time $t + \Delta t$. Then take the total time derivative of F , DF/Dt , with respect to the moving center of mass of the volume element dV , and compare this to $\partial F/\partial t$, taken with respect to the external laboratory axes. Given the position vectors $x(t)$, $y(t)$, and $z(t)$, we then find that

$$\begin{aligned} DF/Dt &= \partial F/\partial t + (\partial F/\partial x)(\partial x/\partial t) + (\partial F/\partial y)(\partial y/\partial t) + (\partial F/\partial z)(\partial z/\partial t) \\ &= \partial F/\partial t + \mathbf{v} \cdot \nabla F. \end{aligned} \quad (6.1.33)$$

The two terms on the right correspond, respectively, to those on the left-hand side of Eq. (6.1.6). The quantity on the left is often written out in the form dF/dt .

Notes and Queries

- 6.1.1. As shown in Section 1.3, where integration limits are variable, one cannot with impunity interchange differentiation and integration operators. The above steps show how to handle this problem for volumes that vary with time.
- 6.1.2. In fact, one may write the first law as $d_e = \widehat{C}_V dT + \sum_k (\mu_k + Ts_k) dc_k$, and recognize that $\mu_k + Ts_k = h_k$ is an enthalpy density of species k contributing to e , which in this case may be regarded as a “heat of reaction”.
- 6.1.3. For a single species, the summations drop out; then the ratio J_U/J_1 may be regarded as the partial molal energy density carried by species 1, U^* ; likewise, J_S/J_1 represents the partial molal entropy carried by species 1, S^* . Equation (6.1.28) then specializes to $U^* - TS^* = \xi$, or, equivalently, to $E - TS^* = \mu$, which is an analog of $H - TS = G$.
- 6.1.4. How are all of the above relationships changed if, instead of dealing with extensive variable per unit volume, one were to switch to “specific” quantities, i.e., extensive variables per unit mass?
- 6.1.5. Construct equations of continuity that explicitly account for the presence of pressure gradients in a system. Consult major treatises on irreversible thermodynamics for an extensive treatment of this subject.

6.2 Shock Phenomena

Introductory Considerations; Small Departures from Equilibrium

As our next illustration of nonequilibrium phenomena, we consider the case of shock effects in conjunction with Figure 6.2.1.

- (i) Let a piston be suddenly accelerated to a velocity u , traveling to the right in the shock tube depicted in Figure 6.2.1. Assuming steady-state conditions, the material to the right of the

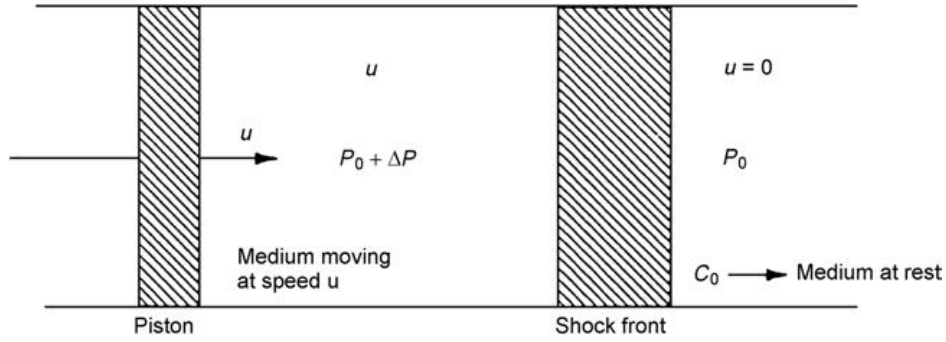


FIGURE 6.2.1

Illustration of the motion of a piston and of a shock front in a shock tube.

piston moves along in the same direction as the piston with the same velocity. The compressed material at pressure $P_0 + \Delta P$ is preceded by a “shock front,” ahead of which is the undisturbed material at pressure P_0 and at rest. The shock front moves with sound velocity c_0 and extends over the region where the pressure changes from P_0 to $P_0 + \Delta P$. The density of the undisturbed material is ρ_0 and that of the region behind the shock front is $\rho_0 + \Delta\rho$.

- (ii) Let an observer ride along the shock front down the tube. He would see material “entering” on the right with velocity c_0 at a density ρ_0 and “leaving” on the left with velocity $c_0 - u$ at a density $\rho_0 + \Delta\rho$. The mass of material processed in this manner must be conserved; per unit time, the mass crossing unit area into the shock front, and the mass leaving unit area at the back of the shock wave, is given by

$$m_t = \rho_0 c_0 = (\rho_0 + \Delta\rho)(c_0 - u). \quad (6.2.1)$$

This relation may be solved for

$$u = c_0 \Delta\rho / (\rho_0 + \Delta\rho). \quad (6.2.2)$$

- (iii) Next, we invoke Newton’s second law of motion: per unit time and cross-section, a mass m_t of material changes its momentum from 0 to $m_t u$; according to Newton’s law, this rate of change in momentum must be accounted for by a force per unit area which changes from P_0 to $P_0 + \Delta P$. Hence,

$$\Delta P = \rho_0 c_0 u. \quad (6.2.3)$$

We eliminate u from Eqs. (6.2.2) and (6.2.3) and solve for

$$c_0^2 = (\rho_0 + \Delta\rho) \Delta P / \rho_0 \Delta\rho. \quad (6.2.4)$$

- (iv) Under the further *assumption* that all disturbances are small, we set $\Delta\rho \ll \rho_0$ and $\Delta P / \Delta\rho = dP/d\rho$, so that

$$dP/d\rho = c_0^2. \quad (6.2.5)$$

Assume next that the compression occurs so rapidly that the material has no time to respond before it is transformed from the undisturbed state to the steady state behind the shock front. In this event, the transformation occurs adiabatically.

- (v) We now specialize to the case where the material under study is an ideal gas. For the small disturbances envisaged in (iv), the temperature is assumed to remain constant, and under adiabatic conditions, $PV^\gamma = \text{constant}$, where $\gamma \equiv \tilde{C}_P/\tilde{C}_V$. Since $V \sim \rho_0^{-1} \sim \rho^{-1}$, the adiabatic condition may be reformulated to read $P = A\rho_0^\gamma \approx P_0$. Then

$$dP/d\rho = \gamma A\rho_0^{\gamma-1} = \gamma P_0/\rho_0, \quad (6.2.6)$$

and in view of Eq. (6.2.5),

$$c_0 = \sqrt{(P_0\gamma/\rho_0)}. \quad (6.2.7)$$

For an ideal gas, $P_0/\rho_0 = RT_0/M$, where T_0 is the temperature of the undisturbed medium and M is the gram molecular mass. Accordingly,

$$c_0 = \sqrt{(\gamma RT_0/M)}. \quad (6.2.8)$$

Note that Eq. (6.2.8) may be inverted to determine γ from a measurement of the velocity of sound. With $\gamma = (C_V + nR)/C_V$, both \tilde{C}_V and \tilde{C}_P may then be found.

Shock Phenomena in Large Departures from Equilibrium

We now generalize considerably by allowing for steady-state conditions extensively removed from equilibrium; this forces us to take into account severe excursions of T , P , ρ , or $v \equiv \rho^{-1}$ from the equilibrium properties T_0 , P_0 , ρ_0 , and $v_0 \equiv \rho_0^{-1}$, respectively. The situation may be visualized with the diagram shown in Figure 6.2.2.

As before, we invoke the conservation law for matter, m_t , being the mass of material that is being overtaken by unit area of the shock front per unit time. Then, in analogy to Eq. (6.2.1),

$$m_t = \rho_0 c = (c - u)\rho, \quad (6.2.9)$$

where c is the velocity of propagation of the shock front. We will later relate this quantity to c_0 ; the two differ because with rising temperatures, the propagation velocities increase.

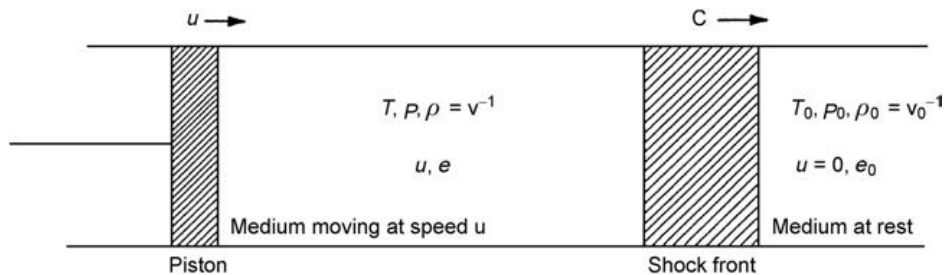


FIGURE 6.2.2

Illustration of the motion of a piston and of a shock front in a shock tube under severe departures from equilibrium.

As was done in conjunction with Eq. (6.2.3), we can set up an equation based on Newton's second law of motion:

$$P - P_0 = \rho_0 c u = m_t u. \quad (6.2.10)$$

Next, we introduce the first law of thermodynamics: let e_0 and e be the energies of the material per unit mass of material being overtaken in unit time by unit area of the shock front (for which $m_t = 1$); the difference $e - e_0$ in energy, before and after the shock wave has hit, must reflect any chemical reactions initiated by the shock. The change in kinetic energy acquired by this quantity of material is $u^2/2$; thus, we write

$$\Delta e = e - e_0 + u^2/2. \quad (6.2.11)$$

The work performed by the piston on the material per unit time and transmitted across units cross-section is Pu . Assuming adiabatic shock conditions, the first law of thermodynamics then states that

$$Pu = m_t(e - e_0 + u^2/2). \quad (6.2.12)$$

Algebraic Manipulations

We have at hand now all the laws needed in our further development; the rest is algebra.

First, solve Eq. (6.2.9) for c :

$$c = \frac{\rho u}{\rho - \rho_0} = \frac{v u}{v - v_0}. \quad (6.2.13)$$

Second, divide Eq. (6.2.12) by Eq. (6.2.10),

$$\frac{Pu}{P - P_0} = \frac{e - e_0 + u^2/2}{u}, \quad (6.2.14)$$

and solve for

$$e - e_0 = \frac{1}{2} [(P + P_0)/(P - P_0)] u^2 \rightarrow u^2/2 \quad \text{for } P \gg P_0. \quad (6.2.15)$$

Third, eliminate c in Eq. (6.2.9) by use of Eq. (6.2.13) and simplify. This yields

$$m_t = u/(v_0 - v). \quad (6.2.16a)$$

Fourth, eliminate m_t via Eq. (6.2.10) and solve the resultant for

$$u^2 = (P - P_0)(v_0 - v). \quad (6.2.16b)$$

Finally, use Eq. (6.2.16b) in Eq. (6.2.15) to obtain

$$e - e_0 = (P + P_0)(v_0 - v)/2, \quad (6.2.17)$$

which is known as *Hugoniot's equation*. If we set $h = e + Pv$, $h_0 = e_0 + P_0v$, we may write

$$h - h_0 = (P - P_0)(v - v_0)/2. \quad (6.2.18)$$

Use of Ideal Gas as a Working Substance

We now specialize considerably by dealing with an ideal gas as a working substance. Then

$$PV = nRT = (m/M)RT, \quad (6.2.19)$$

or

$$Pv = RT/M \quad (6.2.20)$$

and

$$e = c_V T + \text{constant} = (\tilde{C}_V/M)T + \text{constant}. \quad (6.2.21)$$

Use Eq. (6.2.21) on the left and Eq. (6.2.20) on the right of Eq. (6.2.17):

$$\left(\frac{\tilde{C}_V}{M}\right)(T - T_0) = \frac{1}{2}\left(\frac{R}{M}\right)(P + P_0)\left[\frac{T_0}{P_0} - \frac{T}{P}\right]. \quad (6.2.22)$$

Note how e has been eliminated in favor of \tilde{C}_V . We reformulate the above by defining a *shock strength* by $\Pi = P/P_0$, in terms of which we rewrite Eq. (6.2.22) as

$$\tilde{C}_V(T - T_0) = (R/2)(\Pi + 1)(T_0 - T/\Pi). \quad (6.2.23)$$

Then collect terms in T and in T_0 :

$$T(2\tilde{C}_V + R + R/\Pi) = (2\tilde{C}_V + R + \Pi R)T_0, \quad (6.2.24)$$

or

$$\frac{T}{T_0} = \frac{2\tilde{C}_V + R + R\Pi}{2\tilde{C}_V + R + R/\Pi}. \quad (6.2.25)$$

For $\Pi \gg R$, this relation reduces to

$$T/T_0 \rightarrow [R/(2\tilde{C}_V + R)\Pi]. \quad (6.2.26)$$

The factor on the right appears so frequently that we introduce for it a new symbol, $\mu_s \equiv R/(2\tilde{C}_V + R) = R/(\tilde{C}_P + \tilde{C}_V)$. We then obtain

$$\frac{T}{T_0} = \frac{1 + \mu_s \Pi}{1 + \mu_s/\Pi} \rightarrow \mu_s \Pi \quad \text{for } \Pi \gg 1. \quad (6.2.27)$$

At higher T , ignoring the internal degrees of freedom, $\tilde{C}_V = 3R/2$ for a monatomic gas, and $\tilde{C}_V = 5R/2$ for a diatomic gas. Hence, $T/T_0 \rightarrow \Pi/4$ or $\Pi/6$ for monatomic or diatomic gases, respectively. Note the route we took to obtain information on the rise in temperature when an ideal gas is shocked, and note that the asymptotic limits for T/T_0 differ for monatomic and diatomic gases.

Interrelations Involving Shock Phenomena

From the above, we can now establish a considerable number of interrelations using various algebraic manipulations. For instance, are the following:

- (i) We can find the ratio ρ/ρ_0 from

$$\rho/\rho_0 = (P/P_0)(T_0/T) = (\Pi + \mu_s) / (1 + \mu_s \Pi) \quad (6.2.28a)$$

$$\rightarrow 1/\mu_s \text{ for } \Pi \gg 1. \quad (6.2.28b)$$

Thus, there exists a distinct upper limit on ρ/ρ_0 , of 4 and of 6 for monatomic and diatomic gases, for very large shock strengths.

- (ii) Information on the mass flow velocity is obtained by first using Eq. (6.2.21) to determine

$$e - e_0 = (\tilde{C}_V/M)(T - T_0), \quad (6.2.29)$$

and then using this result in Eq. (6.2.15), eliminating T through Eq. (6.2.27), and reintroducing $\Pi \equiv P/P_0$. This yields

$$u^2 = 2 \frac{\tilde{C}_V T_0}{M} \left[\frac{(\Pi - 1)^2}{\Pi + \mu_s} \right] \mu_s, \quad (6.2.30)$$

which shows that in (an ideal) gas, there exists a connection between shock strength and mass flow velocity.

- (iii) We may eliminate T_0 for the undisturbed medium from Eq. (6.2.30) by recalling Eq. (6.2.8) and noting that $\mu_s = R/\tilde{C}_V(1 + \gamma)$; on carrying out the indicated operation and taking square roots of the resultant, we find the following:

$$\frac{u}{c_0} = \left[\frac{2}{\gamma(\gamma + 1)} \frac{(\Pi - 1)^2}{\Pi + \mu_s} \right]^{1/2} \quad (6.2.31a)$$

$$\rightarrow \sqrt{2\Pi/\gamma(\gamma + 1)} \quad (6.2.31b)$$

$$\rightarrow 0.716\sqrt{\Pi} \quad \text{monatomic gas, } \Pi \gg 1 \quad (6.2.31c)$$

$$\rightarrow 0.890\sqrt{\Pi} \quad \text{diatomic gas, } \Pi \gg 1. \quad (6.2.31d)$$

Thus, for Π sufficiently large, $u/c_0 > 1$; i.e., the mass flow velocity becomes supersonic.

(iv) To examine the ratio c/c_0 , we begin with Eq. (6.2.13):

$$\frac{c}{c_0} = (1 - \rho_0/\rho)^{-1} u/c_0 = \frac{\Pi + \mu_s}{(\Pi - 1)(1 - \mu_s)} \left(\frac{u}{c_0} \right), \quad (6.2.32)$$

where Eqs. (6.2.28) had been used. Now substitute for u/c_0 from Eqs. (6.2.31) to obtain

$$\frac{c}{c_0} = \sqrt{\left[\frac{2(\Pi + \mu_s)}{\gamma(\gamma + 1)(1 - \mu_s)^2} \right]}. \quad (6.2.33)$$

This relation may be simplified by noting from the definition of μ_s and γ that $\mu_s = (\gamma - 1)/(\gamma + 1)$; then

$$c/c_0 = \sqrt{\left[(\gamma + 1)/2\gamma (\Pi + \mu_s) \right]} \quad (6.2.34a)$$

$$c/c_0 \rightarrow \sqrt{\left[(\gamma + 1)/2\gamma \Pi \right]} \quad \text{for } \mu_s \gg \Pi. \quad (6.2.34b)$$

$$\rightarrow 0.890\sqrt{\Pi}, \quad \text{for a monatomic gas, } \mu_s \gg \Pi \quad (6.2.34c)$$

$$\rightarrow 0.926\sqrt{\Pi}, \quad \text{for a diatomic gas, } \Pi \gg \mu_s. \quad (6.2.34d)$$

A comparison of Eqs. (6.2.34a,b,c,d) with Eqs. (6.2.31a,b,c,d) establishes that $c > u$; the shock wave will always outrun the mass velocity of the gas. The ratio $c/c_0 \equiv M$ is called the *Mach number*.

Equation of State

We can write a *shock equation of state* by defining $\rho/\rho_0 = v_0/v \equiv \xi_s$. Then Eqs. (6.2.28) may be rearranged to read

$$\Pi = (\xi_s - \mu_s)/(1 - \xi_s \mu_s). \quad (6.2.35)$$

Compare this to the case of the reversible, adiabatic equation of state $\Pi = \xi_s^\gamma$ and to the reduced isothermal equation of state $\Pi = \xi_s$.

Exercises

6.2.1. Derive the following relations involving shocked material:

(a) $m^2 = \rho\rho_0(P - P_0)/\rho - \rho_0$

(b) $u^2 = -(P - P_0)(\rho - \rho_0)/(\rho\rho_0)$

(c) $\mu_s = (\gamma - 1)/(\gamma + 1)$.

6.3 Linear Phenomenological Equations

Simple Phenomenological Equations

We reintroduce here the expression for the local rate of entropy production in an isotropic medium that involves the entropy flux vector, Eq. (6.1.27):

$$\dot{\theta} = -T^{-1} \mathbf{J}_S \cdot \nabla T - T^{-1} \sum_{k=1}^n \mathbf{J}_k \cdot \nabla \zeta_k + \sum_{l=1}^n (\mathcal{A}_l/T) \omega_l \geq 0. \quad (6.3.1)$$

We now introduce several simplifying scenarios, by which we recover the results obtained heuristically in Section 2.2. Consider first the situation where no chemical reactions take place and no particle fluxes occur: $\dot{\theta} = -T^{-1} \mathbf{J}_S \cdot \nabla T \geq 0$, whence $\mathbf{J}_S = \mathbf{J}_Q/T$. Then Eq. (6.3.1) specializes to $\dot{\theta} = -T^{-1} \mathbf{J}_S \cdot \nabla T = \mathbf{J}_Q \cdot \nabla(1/T)$. In our standard interpretation, \mathbf{J}_Q and $\nabla(1/T)$ are conjugate flux–force pairs, so that the heat flux \mathbf{J}_Q is “driven” by the gradient of $1/T$. For small departures from equilibrium, one may assume a linear dependence which is homogeneous, so that no additive constant prevents the flux from vanishing simultaneously with the force $\nabla(1/T)$. In short, we write

$$\mathbf{J}_Q = L \nabla(1/T), \quad (6.3.2a)$$

where $L(T)$ is a scalar function of temperature; a tensor would be inappropriate since this would imply a set of preferred directions. The above may be rewritten as

$$\mathbf{J}_Q = -(L/T^2) \nabla T \equiv -\kappa \nabla T, \quad (6.3.2b)$$

which represents the *Fourier’s Law of heat conduction*; κ is the *thermal conductivity*. We have thus recovered a well-established law.

We now repeat the argument when no temperature gradient prevails, no reactions occur, and where flux of one type of particles takes place. Equation (6.3.1) then specializes to $\dot{\theta} = -T^{-1} \mathbf{J}_i \cdot \nabla \zeta_i \geq 0$. This suggests that a gradient in generalized potential, $\nabla \zeta_i$ is a driving force, to which the $T^{-1} \mathbf{J}_i$ is a response. Assuming small departures from equilibrium, a linear relation of the type

$$\mathbf{J}_i = L'(T) \nabla \zeta_i \quad (6.3.3)$$

is then set up; the extra $-T^{-1}$ factor has been absorbed into the $L'(T)$ coefficient. In the absence of any external fields, ζ_i may be replaced by the chemical potential $\mu_i = \mu_i^0 + RT \ln c_i$ whereby, at fixed T , we obtain

$$\mathbf{J}_i = -D(T, c_i) \nabla c_i. \quad (6.3.4)$$

Here c_i is the concentration of species i , and the quantity RT/c_i has been absorbed into the *diffusion coefficient* D . Equation (6.3.4) is known as *Fick’s Law of diffusion*. The coefficient is clearly concentration dependent. In Eq. (6.3.4), the concentration gradient serves as the “driving force,” but as shown in Eq. (6.3.3), it is the gradient in chemical potential that really activates the particle flow.

If the particle flow involves electrons with charge, $-e$, we recast Eq. (6.3.3) for the charge flux as $\mathbf{J}_e = L''(T) \nabla(\zeta/e)$. Under conditions where the concentration of charge carriers in the volume element is uniform, we may set $\nabla(\zeta/e) = -\nabla\phi$ where ϕ is the electrostatic potential. We then obtain

$$\mathbf{J}_e = L''(T) \nabla(-\phi) = L''(T) \mathbf{E} \equiv \sigma \mathbf{E}, \quad (6.3.5)$$

where $E = -\nabla\phi$ is the electric field vector and σ is the *electrical conductivity*. The above equation represents one formulation of *Ohm's law*.

In the above examples, we have recovered various phenomenological relationships cited in elementary discussions.

Linear Phenomenological Equations

When more than one driving force is operational, one assumes that the *linear superposition principle* holds; that is, every force X_j influences every flux J_j in a linear manner according to the relations

$$\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 + \cdots + L_{1n}X_n \\ J_2 &= L_{21}X_1 + L_{22}X_2 + \cdots + L_{2n}X_n \\ &\vdots \\ J_n &= L_{n1}X_1 + L_{n2}X_2 + \cdots + L_{nn}X_n. \end{aligned} \quad (6.3.6)$$

Expressions of this type are generally known as *phenomenological* or *macroscopic equations*. As discussed in Section 6.1, they are based on the dissipation relation $\dot{\theta} = \sum_j J_j \cdot X_j$, with $1 \leq j \leq n$ sets of conjugate variables. As shown above, every flux is accorded its own phenomenological equation, which additively involves every one of the prevailing forces; every force linearly affects each flux. The various L_{ij} are commonly known as *phenomenological* or *macroscopic coefficients*. Those for which $j = i$ are known as *proper coefficients*; the remainder provide cross-coupling effects between forces of one type and fluxes of another kind, and are known as *interference coefficients*. The validation of the phenomenological equations ultimately rests on the success that such relations provide in an analysis of experimental results. In particular, these equations hold only for “sufficiently small” departures from equilibrium conditions; what “sufficiently small” means can only be established by observing experimental conditions under which these equations fail.

In conjunction with Eq. (6.3.6), we introduce the ORC which will be derived below under a restricted set of circumstances. The ORC read as follows:

$$L_{ij} = L_{ji}. \quad (6.3.7)$$

It is stressed that these relations apply only if the phenomenological equations are based on conjugate force–flux pairs. If other types of pairs are employed, the coefficients with $i \neq j$ are functionally related but not equal.

In the presence of magnetic fields \mathcal{B} and/or in systems undergoing angular rotations at rates ω , the above expression is replaced by the *Casimir–Onsager reciprocity relation*,

$$L_{ij}(\mathcal{B}, \omega) = \pm L_{ji}(-\mathcal{B}, -\omega), \quad (j \neq i), \quad (6.3.8)$$

where the negative sign prevails if the applicable forces change in direction as the field or angular velocity direction is reversed.

6.4 Steady-State Conditions and Prigogine's Theorem

Steady-state conditions obtain when the fluxes and forces giving rise to irreversible phenomena in a system remain time-invariant, while the properties of the surroundings change. We render this concept more precise by introducing *Prigogine's theorem*: let irreversible processes take place

through imposition of n forces X_1, X_2, \dots, X_n that result in n fluxes J_1, J_2, \dots, J_n . Let the first k forces remain fixed at values $X_1^0, X_2^0, \dots, X_k^0$; then it is claimed that the rate of entropy production $\dot{\theta}$ is minimized when the fluxes $J_{k+1}, J_{k+2}, \dots, J_n$ all vanish. We first prove the theorem and then discuss its relevance to steady-state conditions. As before, we set $\dot{\theta} = \sum_j J_i \cdot X_i$, to construct the phenomenological equations,

$$J_i = \sum_j L_{ij} X_j, \quad L_{ij} = L_{ji}, \quad (6.4.1)$$

and the expression

$$\dot{\theta} = \sum_i \sum_j L_{ij} X_i \cdot X_j \geq 0. \quad (6.4.2)$$

An extremum is found by differentiating $\dot{\theta}$ with respect to the nonfixed forces (we ignore niceties involved in differentiating vectorial quantities¹). This leads to the result

$$(\partial \dot{\theta} / \partial X_i)_{X_{i \neq j}} = 0 = \sum_j (L_{ij} + L_{ji}) X_j, \quad (i = k+1, k+2, \dots, n; j = 1, 2, \dots, k). \quad (6.4.3)$$

Note that the local rate of entropy production is a minimum since $\dot{\theta}$ is nonnegative. On introducing Eq. (6.4.1), one obtains

$$2 \sum_j L_{ij} X_j = 2J_i = 0, \quad (6.4.4)$$

which proves the theorem.

In light of the above, the relations specifying J_i with $i = k+1, k+2, \dots, n$ (all of which vanish) may now be solved for the various X_j , as unknowns (where $j = k+1, k+2, \dots, n$) in terms of the fixed X_j^0 , thereby rendering all X_j time-invariant². Accordingly, all of the fluxes J_i either are zero or assume fixed values. But these circumstances are precisely the hallmark of steady-state conditions. We have thus established that *a steady state prevails when the local rate of entropy production is at a minimum with respect to the prevailing constraints*.

Steady-state conditions tend to be inherently stable: consider a case where all forces except one, namely $X_m, k+1 \leq m \leq n$, is held fixed. Now apply a perturbation δX_m to this force; this engenders a nonzero flux $J_m = L_{mm} \delta X_m$ that had previously vanished. Since $\dot{\theta} = L_{mm} (\delta X_m)^2 > 0$, $L_{mm} > 0$. Thus, $J_m \delta X_m > 0$. Now, any flow J_m of a given magnitude brings about a change of opposite sign in the associated conjugate force; this matter is explored in the Comments section. Therefore, the flow J_m cannot be sustained; the system ultimately returns to the quiescent condition. We see that this leads to an application of *Le Châtelier's principle* to steady-state phenomena. Steady-state conditions remain stationary.

Comments and Questions

6.4.1. Examine more closely the proof of Prigogine's theorem and make due allowance for the fact that one must deal properly with vectorial quantities. This may be done by putting the relations into component forms.

- 6.4.2.** This statement is best verified by use of a live example, such as setting $n = 4$ and assuming that the first two forces remain fixed in time. Then carry through the various steps to check the correctness of all assertions.
- 6.4.3.** Discuss the appropriateness of the statement that a flux always occurs in a manner that under steady-state conditions causes a reduction in the conjugate force that maintains it. You may consider as illustrations the flow of a current from an isolated battery, or the passage of matter from an isolated reservoir into the system.

6.5 Onsager Reciprocity Conditions

We provide here a simplified derivation of the ORC that is applicable only when steady-state conditions apply. A full derivation, based on the machinery of statistical mechanics, is not beyond our purview, but would lead us too far afield. Instead, the present derivation, based on Tykodi's work,¹ is sufficient for what follows. In scrutinizing the derivation, you are strongly advised to write out the various steps in full, using three forces and fluxes as an example. We continue to dispense with vectorial notation.

The phenomenological equations will be written in the form shown below, with $i, j = 1, 2, \dots, r$

$$J_1 = \sum_j L_{1j} X_j \quad (6.5.1a)$$

$$\vdots$$

$$J_i = \sum_j L_{ij} X_j \quad (6.5.1b)$$

$$\vdots$$

$$J_k = \sum_j L_{kj} X_j \quad (6.5.1c)$$

$$\vdots$$

$$J_r = \sum_j L_{rj} X_j. \quad (6.5.1d)$$

Now solve Eq. (6.5.1c) for

$$X_k = J_k / L_{kk} - \sum_{j \neq k} (L_{kj} / L_{kk}) X_j. \quad (6.5.2)$$

Substitute this quantity in Eq. (6.5.1b) to obtain

$$J_i = \sum_{j \neq k} L_{ij} X_j + L_{ik} J_k / L_{kk} - \sum_{i \neq k} (L_{ik} L_{kj} / L_{kk}) X_i, \quad (6.5.3)$$

whereby all J_i have now been expressed in terms of J_k and all $X_{j \neq k}$. We next take partial derivatives of the dissipation function $\dot{\theta} = \sum_j J_j X_j$ to obtain

$$\partial \dot{\theta} / \partial J_k = X_k + \sum_{i \neq k} X_i (\partial J_i / \partial J_k) = X_k + \sum_{i \neq k} (L_{ik} / L_{kk}) X_i. \quad (6.5.4)$$

Next, rewrite Eq. (6.5.1c) as $J_k = L_{kk}X_k + \sum_{i \neq k} L_{ki}X_i$, and use this form to eliminate X_k from Eq. (6.5.4). This leads to

$$\partial \dot{\theta} / \partial J_k = J_k / L_{kk} + \sum_{i \neq k} ((L_{ik} - L_{ki}) / L_{kk}) X_i. \quad (6.5.5)$$

Referring to the previous section, we note that when no constraints are imposed, the left-hand side vanishes under steady-state conditions, and all fluxes J_k do likewise. This forces the second term on the right to vanish as well, thereby establishing the ORC in this special case. Again, the present derivation is highly restrictive; however, it is germane to the present and later derivations, and it does furnish a simple proof of a theorem that has been shown to hold under far more general conditions.

Reference

6.5.1. R.J. Tykodi, *Thermodynamics of Steady States* (MacMillan, New York, 1967), pp. 31–33.

6.6 Thermomolecular Mechanical Effects

So far we have set up the basic machinery which permits the principles of irreversible thermodynamics to be applied to problems of interest. We now show how to apply the methodology, using an elementary example. The same approach will be used in subsequent sections, with appropriate variations on a basic theme.

Experimental Conditions

The system under study consists of two vessels at constant volume filled with a single type of fluid and connected by a small opening; the vessels are maintained at two different, uniform pressures and temperatures. We wish to examine the heat and mass flows between the two portions of the system.

Attention is focused on the quantity $\dot{\theta}$ for the rate of change of entropy density due to processes occurring totally within the system. This permits the identification of pairs of conjugate fluxes and forces as prescribed in Section 6.1. We may use one of the two formulations, namely Eqs. (6.1.27) or (6.1.29); other expressions have also been specified in the literature. Select Eq. (6.1.29) for convenience. The fluxes (presently on a molar basis, dropping vectorial notation and tilde symbols) are then taken to be J_U and J_1 , and the corresponding conjugate forces are $\nabla(1/T)$ and $-\nabla(\mu_1/T)$ respectively. We temporarily replace J_U by J_0 and set $\nabla(1/T) \equiv X_0$, $-\nabla(\mu_1/T) \equiv X_1$. The following phenomenological relations now result, valid for fluxes and forces operating along one dimension:

$$J_0 = L_{00}X_0 + L_{01}X_1 \quad (6.6.1a)$$

$$J_1 = L_{10}X_0 + L_{11}X_1. \quad (6.6.1b)$$

Since conjugate force–flux pairs have been selected, Onsager’s reciprocity conditions apply: $L_{01} = L_{10}$.

Reformulation of driving forces

For further progress, it is desirable to recast Eqs. (6.6.1) in terms of experimentally measurable driving forces: we may select as driving forces the quantities, cf. Eq. (6.1.29): $X_0 = -T^2 \nabla T$, as well as

$$\begin{aligned} X_1 &= -\nabla(\mu_1/T) = -T^{-1} \nabla \mu_1 + (\mu_1/T^2) \nabla T = -T^{-1} \left[-\overline{S}_1 \nabla T + \overline{V}_1 \nabla P \right] + (\overline{H}_1 - T \overline{S}_1) T^{-2} \nabla T \\ &= -(\overline{V}_1/T) \nabla P + (\overline{H}_1/T^2) \nabla T. \end{aligned} \quad (6.6.2a)$$

Then, on connecting terms in ∇P and ∇T with J_U and J_1 via coupling coefficients L_{ij} , we write

$$J_U = -L_{01} (\overline{V}_1/T) \nabla P + \left[(L_{01} \overline{H}_1 - L_{00}) / T^2 \right] \nabla T \quad (6.6.2b)$$

$$J_1 = -L_{11} (\overline{V}_1/T) \nabla P + \left[(L_{11} \overline{H}_1 - L_{01}) / T^2 \right] \nabla T. \quad (6.6.2c)$$

The nonuniformities in P and T are encountered only at the junction between the vessels; accordingly, ∇P and ∇T may be replaced by the pressure and temperature differences at the junction, ΔP and ΔT , respectively; the small thickness of the connecting unit may be absorbed in the coefficients L .

Steady-State Conditions

Next, we impose a variety of steady-state conditions on Eqs. (6.6.2) to endow the coefficients with physical interpretations, and to arrive at a variety of predictions.

Suppose first that the temperature is maintained at a uniform value. The sole driving force is now the pressure difference between the vessels. Setting $\nabla T = 0$ and dividing Eq. (6.6.2a) by Eq. (6.6.2b) yields a relation of the form

$$(J_U/J_1)_{\nabla T=0} = L_{01}/L_{11} \equiv U_1^*. \quad (6.6.3)$$

Here J_U is the rate of energy density transfer across unit cross-section in unit time arising from the flux in moles of species 1 across unit cross-section in unit time. This ratio is clearly the energy transported under isothermal conditions per mole of species 1, denoted by U_1^* in Eq. (6.6.3). We see then that a *thermomechanical effect* is predicted: for a fixed pressure difference across the junction, ΔP , and at constant temperature, a particle flux, J_1 , gives rise to a proportional energy transport $J_U = U_1^* J_1$. This is a very sensible conclusion.

Consider next the stationary state under which no mass transfer occurs, but heat flux is permitted. We now set $J_1 = 0$ in Eq. (6.6.2b) and solve for the ratio

$$(\nabla P/\nabla T)_{J_1=0} = \left[(\overline{H}_1 - L_{01}/L_{11}) / \overline{V}_1 T \right] = (\overline{H}_1 - U_1^*) / \overline{V}_1 T \equiv Q_1^* / \overline{V}_1 T, \quad (6.6.4)$$

where the quantity on the right results from use of Eq. (6.6.3); Q_1^* is a molar “heat of transfer,” defined by $\overline{H}_1 - U_1^*$. We thus encounter a second physical prediction: under conditions where mass flow is blocked, a difference in temperature between two vessels, which are allowed to interchange energy, necessarily results in the establishment of a pressure difference $\Delta P = (Q_1^* / \overline{V}_1 T) \Delta T$ between the communicating vessels. This also is a physically sensible prediction.

As a third special case, consider the mass flow resulting from a pressure difference between the two vessels maintained at a uniform temperature. According to Eq. (6.6.2b), this leads to $J_1 = -(L_{11}\overline{V}_1/T)\nabla P$, which is an analog of electric current flow arising from a difference of electrical potential. Accordingly, it is sensible to introduce a *hydraulic permittivity*, Σ , for mass flow, defined as [Why include the minus sign as part of the definition?]

$$-(J_1/\nabla P)_{\nabla T=0} = L_{11}\overline{V}_1/T \equiv \Sigma; \quad J_1 = -\Sigma\nabla P. \quad (6.6.5)$$

Last, it is instructive to determine J_U under conditions of no net mass flow. Accordingly, we set $J_1 = 0$, solve Eq. (6.6.2b) for ∇P , and use this relation to eliminate ∇P in Eq. (6.6.2b). This yields

$$J_U|_{J_1=0} = -(1/T^2 L_{11})(L_{00}L_{11} - L_{10}^2)\nabla T. \quad (6.6.6)$$

The above represents an energy flux arising from the temperature gradient, in the absence of any net particle flow; moreover, under the assumed conditions of constant volume, no work has been performed. The resulting J_U thus is a heat flux; the proportionality coefficient in Eq. (6.6.6) is equivalent to the thermal conductivity, κ . This leads to the identification

$$\kappa = (L_{00}L_{11} - L_{10}^2)/T^2 L_{11}; \quad J_Q = -\kappa\nabla T. \quad (6.6.7)$$

Phenomenological Equations

The analysis may now be completed by collecting Eqs. (6.6.3), (6.6.5), and (6.6.7) and solving these three equations for the three unknowns L_{00} , L_{01} , and L_{11} in terms of κ , Σ , U_1^* or Q_1^* . This yields

$$L_{11} = T\Sigma/\overline{V}_1 \quad (6.6.8a)$$

$$L_{01} = U_1^* T\Sigma/\overline{V}_1 \quad (6.6.8b)$$

$$L_{00} = \kappa T^2 + (U_1^*)^2 T\Sigma/\overline{V}_1. \quad (6.6.8c)$$

When these results are introduced into Eqs. (6.6.2), one obtains a complete phenomenological description of the form

$$J_U = -U_1^* \Sigma \nabla P - \left[\kappa - (U_1^* Q_1^* \Sigma / \overline{V}_1 T) \right] \nabla T \quad (6.6.9a)$$

$$J_1 = -\Sigma \nabla P + (Q_1^* \Sigma / \overline{V}_1 T) \nabla T. \quad (6.6.9b)$$

Equations (6.6.9) show explicitly, in terms of phenomenological coefficients that may be experimentally determined, how the effects of pressure and temperature gradients act jointly in the system to produce concomitant fluxes of energy and of material. All prior information is contained in these relations: if a difference in T is established while no net mass flow is encountered, one recovers the effect predicted by Eq. (6.6.4), and the energy flux is given by Eqs. (6.6.6) and (6.6.7). If uniform temperature is maintained, the mass flux is given by Eqs. (6.6.9) as $J_1 = -\Sigma \nabla P$, and the energy flux, by $J_U = -U_1^* \Sigma \nabla P$. If the pressure is held uniform, one encounters a temperature-driven particle flux $J_1 = (Q_1^* \Sigma / \overline{V}_1 T) \nabla T$ and an energy flux $J_U = -[\kappa - (U_1^* Q_1^* \Sigma / \overline{V}_1 T)] \nabla T$. The superposition effects

established by both forces are formulated through the entire set of Eqs. (6.6.9). A complete analysis of the experimental results has now been furnished.

6.7 Electrokinetic Phenomena

Next, we consider the case depicted in Figure 6.7.1 of a charged membrane (with appropriate counterions in solution) separating two identical electrically neutral solutions maintained at fixed temperature. An electric field or a pressure gradient is now applied, as a result of which both the solvent (water, designated by 0) and positive ions in solution (designated by +) move through the membrane unit until a new steady state has again been achieved. Under the action of the pressure differential, an electrical potential difference is established across the membrane; alternatively, because of the imposition of a potential gradient, a pressure difference is established between the two solutions. The physical situation may be analyzed as shown below.

Phenomenological Equations

As emphasized earlier [see Eq. (6.1.27) and (6.1.29), for example], any flux of charged particles J_+ (on a per mole basis) arises in response to the establishment of a gradient $\nabla\zeta$ in electrochemical potential. For one-dimensional flow, we may write $J_+ = L\nabla\zeta = L(\nabla\mu + Z_+\mathcal{F}\nabla\phi) = L(\bar{V}_+\nabla P + Z_+\mathcal{F}\nabla\phi)$, where the contribution $-\bar{S}dT$ has been dropped because constant-temperature conditions were adopted; similarly, $J_0 = L'\bar{V}_0\nabla P$. Here \mathcal{F} represents the faraday, and Z_+e is the charge on the positive ion.

The compartments R and S in Figure 6.7.1 are assumed to be uniform in properties, so that the changes in P and ϕ occur only across the membrane M . In this case, $\nabla\phi$ and ∇P may be replaced by the discontinuities $\Delta\phi$ and ΔP across the membrane, the constant thickness of the membrane being absorbed into the phenomenological coefficients.

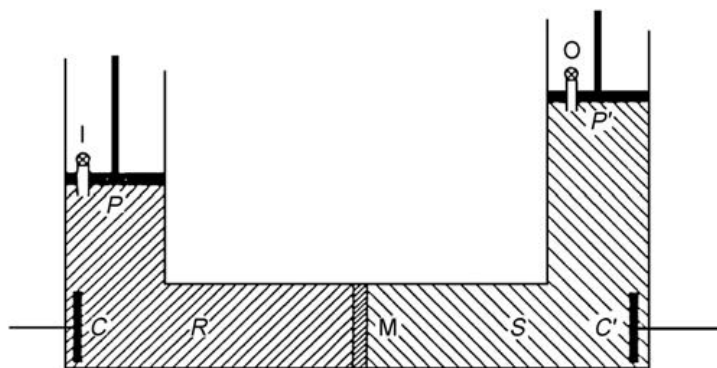


FIGURE 6.7.1

Illustration of apparatus for carrying out electrokinetic experiments. Pressure is applied via movable pistons P and P' on liquids in compartments R and S . Electric fields are generated via condenser plates C and C' . Solvent and positive ions may move through a membrane M separating the compartments. Fluids may be added or removed via stopcocks I and O mounted on the pistons.

The total flux of solvent (J_0) and of ions J_+ is thus given by

$$J_0 = \left(L_{11} \overline{V}_0 + L_{12} \overline{V}_+ \right) \nabla P + L_{12} Z_+ \mathcal{F} \nabla \phi \quad (6.7.1a)$$

$$J_+ = \left(L_{21} \overline{V}_0 + L_{22} \overline{V}_+ \right) \nabla P + L_{22} Z_+ \mathcal{F} \nabla \phi, \quad (6.7.1b)$$

where we have set $L_{11} \equiv L'$, $L_{22} \equiv L$, and where we have taken care of the cross-interactions by introducing the coupling coefficients L_{12} and L_{21} that link J_0 and J_+ to $\nabla \phi$ and to ∇P , respectively. In Exercise 6.7.1, you are asked to show that $L_{12} = L_{21}$.

The preceding phenomenological relations may be rendered symmetric by considering instead of J_0 and J_+ the total volume flow $J_V \equiv \overline{V}_0 J_0 + \overline{V}_+ J_+$ of material and the total current density $\mathcal{J}_+ = Z_+ \mathcal{F}_+$ associated with the ionic transport:

$$J_V = \left[L_{11} \left(\overline{V}_0 \right)^2 + 2L_{12} \overline{V}_+ \overline{V}_0 + L_{22} \left(\overline{V}_+ \right)^2 \right] \nabla P + Z_+ \mathcal{F} \left[L_{12} \overline{V}_0 + L_{22} \overline{V}_+ \right] \nabla \phi \quad (6.7.2a)$$

$$\mathcal{J}_+ = Z_+ \mathcal{F} \left(L_{12} \overline{V}_0 + L_{22} \overline{V}_+ \right) \nabla P + (Z_+ \mathcal{F})^2 L_{22} \nabla \phi, \quad (6.7.2b)$$

which may be abbreviated to read

$$J_V = L_{VV}(-\nabla P) + L_{VI}(-\nabla \phi) \quad (6.7.3a)$$

$$\mathcal{J}_+ = L_{VI}(-\nabla P) + L_{II}(-\nabla \phi). \quad (6.7.3b)$$

Equations (6.7.3) satisfy the ORC, showing that $(J_V, -\nabla P)$ and $(\mathcal{J}_+, -\nabla \phi)$ are sets of conjugate variables. Equations (6.7.3a) and (6.7.3b) are the phenomenological equations of interest.

A later analysis is greatly simplified by generating an inverted set of phenomenological equations, by solving Eqs. (6.7.3) for the gradients in terms of the fluxes:

$$-\nabla P = R_{VV} J_V + R_{VI} \mathcal{J}_+ \quad (6.7.4a)$$

$$-\nabla \phi = R_{VI} J_V + R_{II} \mathcal{J}_+. \quad (6.7.4b)$$

In Exercise 6.7.2, you are asked to determine the various R coefficients in terms of L_{11} , L_{12} , and L_{22} .

Again, these particular relations hold only for constant temperature conditions. If, in addition, no current flow is permitted, then $\mathcal{J}_+ = 0$; according to Eq. (6.7.3b), this imposes the constraint,

$$(\nabla \phi / \nabla P)_{\mathcal{J}_+=0} = -L_{VI} / L_{II}, \quad (6.7.5a)$$

whereas, if no pressure gradient is allowed to develop, i.e., with $\nabla P = 0$, one finds by division of Eq. (6.7.3a) with Eq. (6.7.3b) that

$$(J_V / \mathcal{J}_+)_{\nabla P=0} = L_{VI} / L_{II} \equiv \beta', \quad (6.7.5b)$$

where β' is the so-called *electro-osmotic transfer coefficient*. The quantities on the left of Eqs. (6.7.5a) and (6.7.5b) are termed *streaming potentials* and *electro-osmosis*, respectively. It is immediately evident that

$$(\nabla \phi / \nabla P)_{\mathcal{J}_+=0} = -(J_V / \mathcal{J}_+)_{\nabla P=0}, \quad (6.7.6)$$

which relationship is known as *Saxén's law*.

In Exercise 6.7.3, you are asked to prove that

$$(\nabla P / \nabla \phi)_{J_V=0} = -(\mathcal{J}_+ / J_V)_{\nabla \phi=0}. \quad (6.7.7)$$

Here, the left-hand side is known as the *electro-osmotic pressure*, and the right-hand side, the *streaming current*.

The above relations point up an interesting feature: the streaming potential $(\mathcal{J}_+ / J_V)_{\nabla \phi=0}$ cannot readily be experimentally determined since it forces imposition of a change in electrostatic potential in the absence of a net responding ionic current. However, this quantity is also represented by the ratio $(J_V / \mathcal{J}_+)_{\nabla \phi=0} \equiv \beta'$ which can readily be determined experimentally. Here, one measures the volume flux and current in response to the imposition of a gradient in electrostatic potential when the pressure in the two compartments is identical.

Transport Coefficients

The remainder of this section is devoted to the specification of phenomenological Eqs. (6.7.3) and (6.7.4) by which the coefficients L or R are eliminated in favor of experimentally measurable quantities.

As a first step, solve Eq. (6.7.3b) for $-\nabla \phi$ and substitute the result in Eq (6.7.3a); this yields

$$J_V = (L_{VV} - L_{VI}^2 / L_{II})(-\nabla P) + (L_{VI} / L_{II})\mathcal{J}_+. \quad (6.7.8)$$

Then, for conditions under which no current flow occurs,

$$[J_V / (-\nabla P)]_{\mathcal{J}_+=0} = (L_{VV} - L_{VI}^2) / L_{II} \equiv L_P, \quad (6.7.9)$$

where L_P is the *hydraulic permeability* of the membrane; note that $L_P \geq 0$ [Why?]. This quantity is readily determined experimentally. With $\beta' = (L_{VI} / L_{II})$, Eq. (6.7.8) now reads

$$J_V = L_P(-\nabla P) + \beta'\mathcal{J}_+, \quad (6.7.10)$$

which is known as the first electrokinetic equation.

In conjunction with Eq. (6.7.3b), we define the *membrane conductivity* as

$$\sigma = [\mathcal{J}_+ / (-\nabla \phi)]_{\nabla \phi=0} = L_{II}, \quad (6.7.11)$$

so that with the aid of Eq. (6.7.5b),

$$L_{VI} = \sigma\beta'. \quad (6.7.12)$$

Introduction of Eqs. (6.7.11) and (6.7.12) into Eq. (6.7.3b) yields the *second electrokinetic equation*

$$\mathcal{J}_+ = \sigma\beta'(-\nabla P) + \sigma(-\nabla \phi). \quad (6.7.13)$$

which is simply a reformulation of the second phenomenological equation, Eq. (6.7.3b), in terms of readily measurable quantities. In Exercise 6.7.4, it is to be shown that

$$J_V = (L_P + \sigma\beta'^2)(-\nabla P) + \sigma\beta'(-\nabla \phi), \quad (6.7.14)$$

which is a reformulation of the first phenomenological equation, Eq. (6.7.3a). Note how Eqs. (6.7.9), (6.7.11), and (6.7.12) have been used to solve for the individual L 's in terms of experimental parameters.

In addition to the preceding quantities, the following transport coefficients are in common use: the *steady-state electrical resistivity*

$$\rho|_{J_V=0} = (-\nabla\phi/\mathcal{J}_+)_{J_V=0} = R_H, \quad (6.7.15)$$

where Eq. (6.7.4b) was used to arrive at the relation on the right. To realize this condition, a difference in pressure must be established between the right- and left-hand compartments of Figure 6.7.1 such as to oppose the volume flux J_V normally accompanying the ion flux \mathcal{J}_+ , which itself responds to the imposition of the potential gradient $-\nabla\phi$. In the steady state, the electro-osmotic flux from left to right is counterbalanced by the hydraulic flux from right to left.

The *hydraulic resistance* is defined by

$$R_H \equiv [\nabla P/J_V]_{\mathcal{J}_+=0} = R_{VV}, \quad (6.7.16)$$

where Eq. (6.7.4a) was used to establish the equation on the right.

Finally, in view of Eqns (6.7.4a) and (6.7.5b), the *electro-osmotic flux* may be rewritten as

$$\beta' = [J_V/\mathcal{J}_+]_{\nabla P=0} = -R_{VI}/R_{VV}. \quad (6.7.17)$$

On introducing Eqs. (6.7.15)–(6.7.17) into Eqs. (6.7.4), one obtains final phenomenological equations of the form

$$-\nabla P = R_H J_V - \beta' R_H \mathcal{J}_+ \quad (6.7.18a)$$

$$-\nabla\phi = -\beta' R_H J_V + \rho \mathcal{J}_+, \quad (6.7.18b)$$

which again involve a set of measurable transport coefficients.

All the necessary information relating to electrokinetic phenomena is contained in the phenomenological Eqs. (6.7.13) and (6.7.14) or in the equivalent set Eqs. (6.7.18a) and (6.7.18b). The former set is especially useful if one inquires about state conditions under which either J_V or \mathcal{J}_+ is held fixed. The latter set is useful to characterize operating conditions at constant pressure or constant electrostatic potential. The preceding discussion illustrates the flexibility of phenomenological equations that permit either fluxes or forces to be used as dependent variables.

Exercises

- 6.7.1.** Prove that the phenomenological coefficients in Eqs. (6.7.1) satisfy the ORC.
- 6.7.2.** Express the various coefficients L of Eqs. (6.7.3) in terms of the coefficients R in Eqs. (6.7.4).
- 6.7.3.** Derive Eq. (6.7.7).
- 6.7.4.** Derive Eq. (6.7.14).
- 6.7.5.** From Eqs. (6.7.4b) and (6.7.9), obtain a relation between R_{VI} and L_P .
- 6.7.6.** Discuss the physical mechanism that gives rise to the first electrokinetic equation.
- 6.7.7.** Characterize the steady state of the system when (a) there is no net current flow; (b) there is no net volume flow; (c) the pressure is uniform; and (d) the electrostatic potential is uniform.
- 6.7.8.** Provide an explicit relation for the rate of dissipation of entropy for the general operation of the system and for each of the four cases cited in the preceding exercise.

6.8 The Soret Effect

As the third application of irreversible thermodynamics, we consider the *Soret effect* (1893) for a two-component system characterized by mole fractions x_1 and x_2 when a temperature gradient is imposed on the system: a flow of these components under these conditions produces a gradient in their concentrations. We investigate the magnitude of this effect under steady-state conditions, for which it is expedient to adopt Eq. (6.1.27). It is important to note that while temperature T and mole fractions $x_{1,2}$ are independent variables, they vary with position r within the system. Accordingly, we consider $J_0 \equiv J'_S, J_1, J_2$ to be the entropy and particle fluxes in response to three generalized conjugate forces, namely $X_0 = -T^{-1}\nabla T$ and $X_{1,2} = -T^{-1}\nabla\mu_{1,2}$, as prescribed by Eq. (6.1.27).

The phenomenological equations in the molar representation then assume the form

$$J_0 = L_{00}X_0 + L_{01}X_1 + L_{02}X_2 \quad (6.8.1a)$$

$$J_1 = L_{10}X_0 + L_{11}X_1 + L_{12}X_2 \quad (6.8.1b)$$

$$J_2 = L_{20}X_0 + L_{21}X_1 + L_{22}X_2. \quad (6.8.1c)$$

Note first that even in the absence of a temperature gradient, a flux of entropy and matter can occur. For, when $X_0 = 0$, $J_i = L_{i1}X_1 + L_{i2}X_2$, where $i = 0, 1$, and 2 . At constant temperature, let us define S'_1 and S'_2 as the entropy *intrinsic to* (i.e., exclusive of entropy transport) 1 mol of species 1 and 2. Then at constant T , the entropy flux is given by the postulated form

$$J_0 = S'_1 J_1 + S'_2 J_2 \quad (T \text{ constant}). \quad (6.8.2)$$

On insertion of the appropriate phenomenological equations, this yields

$$J_0 = (S'_1 L_{11} + S'_2 L_{21})X_1 + (S'_1 L_{12} + S'_2 L_{22})X_2. \quad (6.8.3)$$

Comparison with $J_0 = L_{01}X_1 + L_{02}X_2$ at constant T allows one to identify the coefficients of X_1 and X_2 and to solve the resulting linear equations for

$$S'_1 = (L_{01}L_{22} - L_{02}L_{12}) / (L_{11}L_{22} - L_{12}^2) \quad (6.8.4a)$$

$$S'_2 = (L_{02}L_{11} - L_{01}L_{12}) / (L_{11}L_{22} - L_{12}^2). \quad (6.8.4b)$$

Now apply the steady-state condition under which $J_1 = J_2 = 0$, eliminate the constraint of fixed T , and allow X_0 to have a fixed, nonzero value. On eliminating X_2 between Eqs. (6.8.1b) and (6.8.1c), one may solve for the ratio

$$X_1/X_0 = (L_{12}L_{20} - L_{10}L_{22}) / (L_{11}L_{22} - L_{12}^2). \quad (6.8.5)$$

When introducing the earlier representations for X_0 and X_1 and Eq. (6.8.4a), we find that

$$\nabla\mu_1|_T = -S'_1 \nabla T. \quad (6.8.6)$$

Here $\nabla\mu_1|_T$ is the gradient of the chemical potential of species 1 with respect to position coordinates; this relation reads $\nabla\mu_1 = (\partial\mu_1/\partial x_1)_T(\partial x_1/\partial r)$; on insertion into Eq. (6.8.6), one obtains

$$(\partial\mu_1/\partial x_1)_T(\partial x_1/\partial r) = -S_1'^* (\partial T/\partial r), \quad (6.8.7a)$$

or

$$(\partial\mu_1/\partial r)_T = -S_1'^* (\partial T/\partial r), \quad (6.8.7b)$$

which is the expression for the *Soret effect*. This is a new, perhaps unexpected, prediction based on irreversible thermodynamics: in a closed system at constant temperature, a heat flow arising from a temperature gradient under steady-state conditions must produce a gradient in chemical potential with respect to position coordinate r . For an ideal gas, Eqs. (6.8.7) may be reformulated as

$$d \ln x_1|_T = -(S_1'^*/RT)dT. \quad (6.8.8)$$

This analytic relation shows how the mole fraction for component 1 in a two-component ideal gas system is changed by temperature differences prevailing under the assumed steady-state condition. For the special case considered here, an integration leads to

$$\ln(x_1/x_1^0) = - \int_{T_0}^T (S_1'^*/Rt)dt. \quad (6.8.9)$$

If the dependence of $S_1'^*$ on T is sufficiently weak, one finds

$$\ln(x_1/x_1^0) = -(S_1'^*/R)\ln(T/T_0), \quad (6.8.10)$$

with $S_1'^*$ the entropy that is intrinsic to 1 mol of species 1, suitably averaged over the temperature interval T_0 to T . One thereby determines the relative change in gas composition as a function of the relative temperature.

Exercises

- 6.8.1.** Provide a physical mechanism which explains on a microscopic level the thermodynamic result of Eqs. (6.8.7).
- 6.8.2.** Specialize the derivation of this section to a single gaseous species. Show that under steady-state conditions, a temperature gradient produces a pressure gradient and express the magnitude of the latter in terms of the former.

6.9 Thermoelectric Effects

In this section, irreversible thermodynamics will be used to establish the interrelation between heat flow and electric current in a conductor. The field of thermoelectric effects has been treated elsewhere in great detail.¹

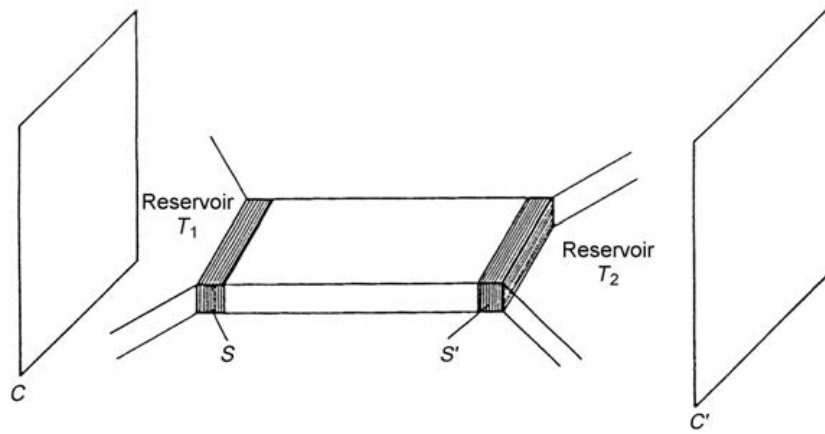


FIGURE 6.9.1

Experimental set up for thermoelectric measurements. A bar is clamped between two reservoirs maintained at different temperatures T_1 and T_2 . S and S' represent the two removable strips used for thermal insulation of the bar. Current is caused to flow in the bar by continuous charging of condenser plates C and C' (see discussion in text).

Consider a rectangular bar (Figure 6.9.1) that is connected to two thermal reservoirs maintained at different temperatures. Provision is made for adiabatic insulation of the sample, if needed. Electrons may be made to flow through the bar in the same direction as the flow of heat (or in the opposite direction) by gradually charging an external set of condenser plates. This cumbersome method is introduced here to avoid the use of electrical wire connections; these lead to distracting complications at junctions between the bar and the current leads. We are interested in the flow of charge and of heat along the bar and in any resulting interference effects.

Phenomenological Relations

According to Section 6.1, an appropriate choice of conjugate fluxes and forces for the present situation is based on the dissipation function, Eq. (6.1.27), specified by $\dot{\theta} = -T^{-1}J_s \cdot \nabla T - T^{-1}J_i \cdot \nabla \zeta_i$, where J_i is the electron flux vector, ζ_i is the electrochemical potential acting on the electron flux, and J_s represents the total entropy density flux vector. We choose this expression, rather than a version based on Eq. (6.1.29), because we wish to treat separately the effects of temperature and of electrochemical potential. The latter involves all the contributions associated with temperature gradients, electron density gradients, and the externally imposed electrostatic field. It is expedient to introduce a *current density vector* as $J_n \equiv -eJ_i$. Then, along one dimension, we adopt $\dot{\theta} = -T^{-1}\mathcal{J}_s \cdot \nabla T + T^{-1}\mathcal{J}_i \cdot \nabla(\zeta/e)$ as our dissipation function. For this unidirectional flow pattern, the phenomenological relations thus read

$$\mathcal{J}_s = -(L_{ss}/T)\nabla T + (L_{sn}/T)\nabla(\zeta/e) \quad (6.9.1a)$$

$$\mathcal{J}_n = -(L_{ns}/T)\nabla T + (L_{nn}/T)\nabla(\zeta/e). \quad (6.9.1b)$$

Identification of Phenomenological Coefficients; Ohm's Law

To replace the phenomenological coefficients with transport parameters, we first consider the special case $\nabla T = 0$. After eliminating $\nabla(\zeta/e)$ between Eqs. (6.8.1a) and (6.8.1b), we obtain $\mathcal{J}_s/\mathcal{J}_n = L_{sn}/L_{nn}$; but since $\mathcal{J}_s/\mathcal{J}_i \equiv S_e^* = -e\mathcal{J}_s/\mathcal{J}_n$ is the total entropy S_e^* carried per particle (including both the intrinsic and the transported portion) at constant temperature, we can set

$$\mathcal{J}_s/\mathcal{J}_n|_{\nabla T=0} = L_{sn}/L_{nn} = -S_e^*/e = L_{ns}/L_{nn} \quad (6.9.2)$$

Next, examine Eq. (6.9.1b); when $\nabla T = 0$, $\mathcal{J}_n = (L_{nn}/T)\nabla(\zeta/e)$. For a homogeneous sample at constant temperature, this latter relation reduces to $\mathcal{J}_n = (L_{nn}/T)\mathcal{E}$ where $\mathcal{E} = -\nabla\phi$ is the electrostatic field. This relation represents a particular case of *Ohm's Law* (1826), $\mathcal{J}_n = \sigma\mathcal{E}$,

$$L_{nn}/T = \sigma, \quad (6.9.3a)$$

where σ is the *electrical conductivity* of the specimen. The more general version,

$$\mathcal{J}_n = \sigma\nabla(\zeta/e), \quad (\nabla T = 0), \quad (6.9.3b)$$

is an elaboration of Ohm's Law that applies to chemically inhomogeneous samples at constant temperature.

Heat Transport; Fourier's Law

Next, examine the case where no current flows: Set $\mathcal{J}_n = 0$ in Eq. (6.9.1b) and then substitute for $\nabla(\zeta/e)$ in Eq. (6.9.1a). This yields

$$\mathcal{J}_s = -(1/T)[L_{ss} - L_{ns}^2/L_{nn}]\nabla T \quad (\mathcal{J}_n = 0). \quad (6.9.4)$$

Entropy flux in the absence of a net particle flow is equivalent to $\mathcal{J}_s = \mathcal{J}_q/T$, where \mathcal{J}_q is the heat flux. Thus, Eq. (6.9.4) is a formulation of Fourier's Law for heat conduction, $\mathcal{J}_q = -\kappa\nabla T$, thereby identifying the *thermal conductivity* associated with the transport of charge carriers as

$$\kappa = L_{ss} - L_{ns}^2/L_{nn}. \quad (6.9.5)$$

In the more general case, one may again eliminate $\nabla(\zeta/e)$ between Eqs. (6.9.1a) and (6.9.1b) to obtain, in view of Eqs. (6.9.2) and (6.9.5),

$$\mathcal{J}_s = -(S_e^*/e\mathcal{J}_n) - (\kappa/T)\nabla T = S_e^*J_i - (\kappa/T)\nabla T, \quad (6.9.6)$$

which shows how the total entropy flux is composed of contributions associated with the temperature gradient and with the particle flux or the current flow. To the thermal conductivity κ of the charge carrier response, we should also add the lattice contribution κ_L , but we will leave this to you to carry along.

Thermoelectric Effects

For another important physical prediction, return again to Eq. (6.9.1b) and set $\mathcal{J}_n = 0$ which also implies that there is no externally applied electric field. One then obtains

$$\nabla(\zeta/e)/\nabla T|_{\mathcal{J}_n=0} \approx d(\zeta/e)/dT|_{\mathcal{J}_n=0} \equiv \alpha = L_{ns}/L_{nn}. \quad (6.9.7)$$

This expression shows that the imposition across the sample of a temperature difference dT in the absence of any current produces a difference $d\zeta$ in electrochemical potential; i.e., $d(\zeta/e) = \alpha dT$. This effect is known as the *thermoelectric effect*, and the ratio $d(\zeta/e)/dT|_{j_n=0} \approx \Delta(\zeta/e)/\Delta T|_{j_n=0} \equiv \alpha$ is known as the *Seebeck coefficient* (1823), or *thermoelectric power*.^{2,3} Experimentally, the difference of electrochemical potential so developed may be measured by a voltmeter under open circuit conditions, and dT , measured by means of thermocouples; α is thereby experimentally determined. Comparison with Eq. (6.9.2) shows that $\alpha = -S_e^*/e$. Physically this effect arises because electrons at the hot end of the sample have a greater thermal energy than those at the cold end and thus tend to move toward the cold end in greater numbers than those at the cold end moving in the opposite direction. See also Note 6.9.2.

According to the above, Eq. (6.9.6) reads

$$\mathcal{J}_s = \alpha \mathcal{J}_n - (\kappa/T) \nabla T, \quad (6.9.8)$$

which shows the additive effects involving the contributions from the current and heat flow.

Phenomenological Equations; Generalizations of Ohm's and Fourier's laws

Finally, we may rewrite the phenomenological equations as follows: since $L_{nn}/T = \sigma$ and $L_{ns}/L_{nn} = \alpha$, Eqs. (6.9.1) becomes

$$\mathcal{J}_n = -\sigma \alpha \nabla T + \sigma \nabla(\zeta/e); \quad (6.9.9a)$$

use of this in Eq. (6.9.8) yields

$$\mathcal{J}_s = -(\sigma \alpha^2 + \kappa/T) \nabla T + \sigma \alpha \nabla(\zeta/e). \quad (6.9.9b)$$

The phenomenological Eqs. (6.9.1) have thus been reexpressed⁴ solely in terms of the measurable transport coefficients σ , κ , and α . The Seebeck coefficient is equal to the entropy carried per electronic charge. Equation (6.9.9a) represents a further generalization of Ohm's Law, showing how the current density depends on both the gradient of electrochemical potential and on the temperature gradient. Equation (6.9.9b) specifies the entropy flux under the joint action of a gradient in electrochemical potential and in temperature; this represents a generalization of Fourier's Law.

Thermoelectric effects in Anisotropic Media

We briefly investigate thermoelectric effects in anisotropic media. For background information, consult Sections 5.10 and 5.11. The phenomenological Eqs. (6.9.1) now assume the following component forms in terms of the repeated index summation convention (for ease of notation some earlier subscripts are now replaced by superscripts):

$$J_i^S = -\frac{L_{ik}^{ss}}{T} \left(\frac{\partial T}{\partial x_k} \right) + \frac{L_{ki}^{sp}}{T} \left(\frac{\partial \zeta/e}{\partial x_k} \right) \quad (i, k = 1, 2, 3 \text{ for } x, y, z) \quad (6.9.10)$$

$$J_i = -\frac{L_{ik}^{ps}}{T} \left(\frac{\partial T}{\partial x_k} \right) + \frac{L_{ik}^{pp}}{T} \left(\frac{\partial \zeta/e}{\partial x_k} \right),$$

where the ki vs ik index notation in the off-diagonal elements must be carefully noted. Again, in view of the range of the free index i , Eqs. (6.9.10) are really the schematic representation of $3 + 3$ equations for the entropy flux and current density, each equation involving three thermal and three electrochemical gradients that represent the driving forces.

We obviously need a shorthand representation. Let \vec{J} represent the column vector (i.e., the transpose of a flux vector \vec{J}^T with components $[J_1, J_2, J_3]$), and let $\vec{\nabla}$ represent the column vector for the gradient (i.e., the transpose of $\vec{\nabla}^T$ whose components are $[\partial/\partial x_1, \partial/\partial x_2, \partial/\partial x_3]$). Further, let \overleftrightarrow{L} represents the matrix of the various $L_{ik} = L_{ki}$ entries of Eqs. (6.9.10). Then, as may be verified by writing out all terms of Eqs. (6.9.10) explicitly, the phenomenological equations assume the form

$$\begin{aligned}\vec{J}^S &= -\left(\overleftrightarrow{L}^{ss}/T\right)\vec{\nabla}T + \left(\overleftrightarrow{L}^{sn}/T\right)\vec{\nabla}(\zeta/e) \\ \vec{J} &= -\left(\overleftrightarrow{L}^{ns}/T\right)\vec{\nabla}T + \left(\overleftrightarrow{L}^{nn}/T\right)\vec{\nabla}(\zeta/e).\end{aligned}\quad (6.9.11)$$

In general, the off-diagonal matrices are not symmetric. Since at fixed temperature the components of \vec{J} are proportional to the components of the tensor $\vec{\nabla}(\zeta/e)$, one deduces that the corresponding coefficients are identical with σ_{ik} , the electrical conductivity tensor entries. One may thus solve for

$$\vec{\nabla}(\zeta/e) = T\left(\overleftrightarrow{L}^{nn}\right)^{-1}\vec{J} + \left(\overleftrightarrow{L}^{nn}\right)^{-1}\overleftrightarrow{L}^{ns}\vec{\nabla}T, \quad (6.9.12)$$

and insert this relation in the first equation of Eq. (6.9.11) to find

$$\vec{J}^S = \left(\overleftrightarrow{L}^{sn}/T\right)(\sigma)^{-1}\vec{J} - \left[\left(\overleftrightarrow{L}^{sn}/T\right)(\sigma)^{-1}\overleftrightarrow{L}^{ns} - \left(\overleftrightarrow{L}^{ss}/T\right)\right]\vec{\nabla}T. \quad (6.9.13)$$

Inspection shows that at fixed temperature, the coefficient of \vec{J} represents entries to the tensor— \vec{S}^*/e , that indicate the transport entropy carried by the electrical species in motion. In the absence of current flow, the coefficient linking $T\vec{J}^S$ to $\vec{\nabla}T$ represents the thermal conductivity tensor associated with the motion of charge carriers. Thus,

$$\kappa = -\overleftrightarrow{L}^{sn}(\sigma)^{-1}\overleftrightarrow{L}^{ns} + \overleftrightarrow{L}^{ss}. \quad (6.9.14)$$

Last, in the absence of current, one may solve Eqs. (6.9.12) for

$$\vec{\nabla}(\zeta/e) = \left(\overleftrightarrow{L}^{nn}\right)^{-1}\overleftrightarrow{L}^{ns}\vec{\nabla}T = \alpha\vec{\nabla}T, \quad (6.9.15)$$

where the indicated coefficient represents the thermoelectric effect or Seebeck coefficient.

Clearly, the specification of the various coefficients requires vastly more experimental information than is needed when isotropic conditions prevail.

Comments and Exercises

- 6.9.1. See e.g., T.C. Harman and J.M. Honig, *Thermoelectric and Thermomagnetic Effects and Applications* (McGraw-Hill, New York, 1967). The presentation given here is of limited (but nevertheless, didactic) utility since it applies only to a metal that is modeled in the free-electron approximation or to extrinsic semiconductors. For more complicated models, particularly those involving charge transport by electrons and holes in multiband materials, the more elaborate analysis presented in advanced treatises is required.
- 6.9.2. The Seebeck coefficient is actually a negative quantity because under the effects of a temperature difference, electrons accumulate at the end of the sample locked onto the cold reservoir, and a deficit of electrons (equivalent to a set of positive charges) develops at the hot end. This is because electrons at the hot end have larger kinetic energies than those at the cold end; they thus tend to migrate toward the latter region to a greater extent than the cold electrons migrating to the hot end. Thus, the direction of the positive temperature gradient is opposite to that of the electron density gradient. If one deals with p -type charge carriers in an extrinsic semiconductor, holes accumulate at the cold end. Now both the T gradient and the electrochemical potential gradient $\nabla\zeta$ for electrons (which is the quantity invoked in the definition for α) point in the same direction, whence α is positive.
- 6.9.3. This particular appellation is highly undesirable and should be eliminated in favor of the designation as *Seebeck coefficient*. Note that the cross-coefficients in the phenomenological Eqs. (6.9.1) as written differ in sign for n -type material. However, if we had adopted $\nabla(\zeta_n/-e)$ as the force conjugate to \mathcal{J}_n , as well as the defining relation $\nabla(\zeta_n/-e)/\nabla T = \alpha_n$, then the ORC conditions would have been satisfied and the phenomenological equations for both electrons and holes would have been identical. The proof of this statement is left as an exercise.
- 6.9.4. How (if at all) must the above approach be modified to deal with transport of positive and negative ions in a solution?
- 6.9.5. Provide a more detailed rationale for the physical origin of the thermoelectric effect by noting the difference in kinetic energy of the charge carriers at the two ends of the sample.
- 6.9.6. Introduce E^* as the internal energy carried by an electron moving under the influence of an external electrostatic field. Relate this quantity to the transport coefficients L_{ss} , L_{ns} , and L_{nn} , and thence, to the transport coefficients introduced in this section.
- 6.9.7. Consider thermoelectric measurements that are carried out under reversible adiabatic conditions for which $\mathcal{J}_s = 0$. Relate the resulting electrical conductivity and Seebeck coefficient to the quantities introduced above.

6.10 Irreversible Thermomagnetic Phenomena in Two Dimensions

In this section, we consider effects arising in conjunction with the geometry illustrated in Figure 6.10.1. A rectangular slab is aligned with the x - and y -axes of a Cartesian coordinate system, and a

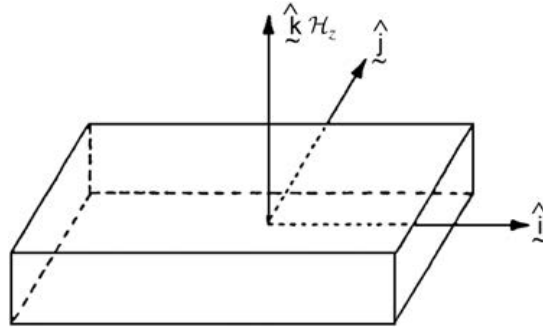


FIGURE 6.10.1

Parallelepiped geometry for current/heat/entropy flux along the $\hat{i}(x)$ and $\hat{j}(y)$ directions in the presence of a magnetic field \mathcal{H}_z aligned with the z direction.

magnetic field \mathcal{H}_z is directed along the z -axis. Provision is made for flux of current and of heat along x and y . One is interested in the possible interference effects. This leads to a consideration of what are termed *thermoelectric* and *thermomagnetic* phenomena; the magnetic field will be shown to give rise to a host of new cross-interactions between processes occurring along the x - and y -directions.

To facilitate the exposition, a somewhat different approach will be used relative to the methods introduced in the earlier sections. Similar to the procedure of Eqs. (6.9.1), we select $(J_s, \nabla T)$ and $(J, \nabla(\zeta/e))$ as the conjugate set of variables, but will absorb the minus signs and the T^{-1} factors in the phenomenological coefficients. Since we deal with electron flow effects we consider J to be the electron current (designated by J_n in Section 6.9) driven by the gradient in electrochemical potential $\nabla(\zeta/e)$ for electrons.

Three new points are introduced at this time. (i) Since fluxes may occur in two orthogonal directions, the conjugate flux–force pairs now are $(J_s^x, \nabla_x T)$, $(J_s^y, \nabla_y T)$, $(J_x, \nabla_x T)$, $(J_y, \nabla_y T)$. (ii) For later convenience, we shall select as independent variables from this particular set the quantities $\nabla_x T$, $\nabla_y T$, J_x , J_y , so that the phenomenological equations appear in partially inverted form as follows:

$$J_s^x = -L_{11}\nabla_x T - L_{12}\nabla_y T + L_{13}J_x + L_{14}J_y \quad (6.10.1a)$$

$$J_s^y = -L_{12}\nabla_x T - L_{11}\nabla_y T + L_{14}J_x + L_{13}J_y \quad (6.10.1b)$$

$$\nabla_x(\zeta/e) = L_{13}\nabla_x T + L_{14}\nabla_y T + L_{33}J_x + L_{34}J_y \quad (6.10.1c)$$

$$\nabla_y(\zeta/e) = -L_{14}\nabla_x T + L_{13}\nabla_y T - L_{34}J_x + L_{33}J_y, \quad (6.10.1d)$$

where the L_{ij} are appropriate phenomenological coefficients. (iii) For later convenience, we have arbitrarily selected the minus and plus signs in the indicated sequence in Eq. (6.10.1a); the other signs in Eqs. (6.10.1) are then governed by the Casimir–Onsager reciprocity conditions, Eq. (6.3.8), as required by the presence of a magnetic field $\mathcal{H} = \hat{k}\mathcal{H}_z$.

We now engage in a systematic treatment of the thermodynamics of irreversible processes in the above configurations. Consider first the isothermal case summarized by the constraints: (a) $J_y = \nabla_x T = \nabla_y T = 0$; isothermal conditions are maintained along x and y , and no current is allowed to flow along y . Then Eqs. (6.10.1) reduce to

$$J_s^x = L_{13}J_x \quad (6.10.2a)$$

$$J_s^y = -L_{14}J_x \quad (6.10.2b)$$

$$\nabla_x(\zeta/e) = L_{33}J_x \quad (6.10.2c)$$

$$\nabla_y(\zeta/e) = -L_{34}J_x. \quad (6.10.2d)$$

According to Eqs. (6.10.2c) and (6.10.2d), current flow along x responds to a gradient in electrochemical potential along both x and y . The first effect simply represents the Ohm's law $J_x = \rho_I \nabla_x(\zeta/e)$, wherein $\rho_I = L_{33}$ is the *isothermal resistivity*. The second is an example of the *isothermal Hall effect*, characterized by

$$\nabla_y(\zeta/e) = -(L_{34}/\mathcal{H}_z)J_x\mathcal{H}_z \quad (6.10.3a)$$

$$\equiv \mathcal{R}_I J_x \mathcal{H}_z, \quad (6.10.3b)$$

wherein, for convenience, the magnitude of the applied magnetic field has been introduced explicitly. As Eq. (6.10.3b) shows, a flow of current longitudinally induces a transverse gradient in electrochemical potential. The magnitude of this effect is specified by the *Hall coefficient*, defined as $\mathcal{R}_I = -(L_{34}/\mathcal{H}_z)$.

We next consider the constraints (b): $J_y = \nabla_x T = J_s^y = 0$. No current flow is allowed along y and no heat flow is tolerated in this direction. Isothermal conditions are maintained along x . This represents a (transverse) adiabatic set of operating conditions. Equations (6.10.1) now reduce to

$$J_s^x = -L_{12}\nabla_y T + L_{13}J_x \quad (6.10.4a)$$

$$0 = -L_{11}\nabla_y T - L_{14}J_x \quad (6.10.4b)$$

$$\nabla_x(\zeta/e) = L_{14}\nabla_y T + L_{33}J_x \quad (6.10.4c)$$

$$\nabla_y(\zeta/e) = L_{13}\nabla_y T - L_{34}J_x, \quad (6.10.4d)$$

Equation (6.10.4b) shows that current flow along x produces a temperature gradient along y ; this is the so-called *Ettingshausen effect*, specified by

$$\nabla_y T = -(L_{14}/(L_{11}\mathcal{H}_z))J_x\mathcal{H}_z \quad (6.10.5a)$$

$$\equiv \mathcal{T} J_x \mathcal{H}_z, \quad (6.10.5b)$$

in which $\mathcal{T} = \nabla_y T / J_x \mathcal{H}_z$ is the *Ettingshausen coefficient*. On inserting Eq. (6.10.5a) into Eq. (6.10.4c), one finds

$$\nabla_x(\zeta/e) = (L_{33} - L_{14}^2/L_{11})J_x, \quad (6.10.6)$$

which is the Ohm's Law under adiabatic conditions, with an *adiabatic resistivity* $\rho_A = L_{33} - L_{14}^2/L_{11}$. When Eq. (6.10.5a) is introduced in Eq. (6.10.4d), one obtains the expression

$$\nabla_y(\zeta/e) = -(1/\mathcal{H}_z)(L_{34} + L_{13}L_{14}/L_{11})(J_x\mathcal{H}_z), \quad (6.10.7a)$$

which represents the *adiabatic Hall effect*, with the *Hall coefficient*

$$\mathcal{R}_A \equiv -(1/\mathcal{H}_z)(L_{34} + L_{13}L_{14}/L_{11}). \quad (6.10.7b)$$

We next consider conditions (c): $J_x = J_y = \nabla_y T = 0$. No current flow is permitted, but a temperature gradient is established along x , while isothermal conditions are maintained along y . The phenomenological equations reduce to

$$J_s^x = -L_{11}\nabla_x T \quad (6.10.8a)$$

$$J_s^y = L_{12}\nabla_x T \quad (6.10.8b)$$

$$\nabla_x(\zeta/e) = L_{13}\nabla_x T \quad (6.10.8c)$$

$$\nabla_y(\zeta/e) = -L_{14}\nabla_x T = -(L_{14}/\mathcal{H}_z)\mathcal{H}_z\nabla_x T, \quad (6.10.8d)$$

Under the postulated conditions, TJ_s^x and TJ_s^y represent heat fluxes. Then Eq. (6.10.8a) leads directly to the definition of an “isothermal heat flux” (a contradiction of terms!): $TJ_s^x = -L_{11}T\nabla_x T$, whence we may write

$$\kappa_I = TL_{11}, \quad (6.10.9)$$

where κ_I is the *thermal conductivity* when no transverse temperature gradient is tolerated. According to Eq. (6.10.8c), a longitudinal temperature gradient produces a longitudinal gradient in electrochemical potential. This represents nothing other than the “isothermal” *Seebeck effect*, introduced in Section 6.9. Thus, with $\nabla_x(\zeta/e) = L_{13}\nabla_x T$, one finds the relation

$$\alpha_I = L_{13}, \quad (6.10.10)$$

where α_I is the Seebeck coefficient in the absence of a transverse temperature gradient. Next, according to Eq. (6.10.8d), a temperature gradient along the x direction produces a gradient of ζ/e along the y direction; this represents the *transverse Nernst effect*: set $\nabla_y(\zeta/e) = -(L_{14}/\mathcal{H}_z)\mathcal{H}_z\nabla_x T$, which suggests defining a corresponding *transverse Nernst coefficient* as

$$\mathcal{N}_I = -L_{14}/\mathcal{H}_z. \quad (6.10.11)$$

Another set of operational conditions frequently encountered is specified by (d): $J_x = J_y = J_s^y$. Here, no currents are allowed to flow, and adiabatic conditions are imposed along the y -direction. Then the phenomenological relations (6.10.1) reduce to

$$J_s^x = -L_{11}\nabla_x T - L_{12}\nabla_y T \quad (6.10.12a)$$

$$0 = L_{12}\nabla_x T - L_{11}\nabla_y T \quad (6.10.12b)$$

$$\nabla_x(\zeta/e) = L_{13}\nabla_x T + L_{14}\nabla_y T \quad (6.10.12c)$$

$$\nabla_y(\zeta/e) = L_{14}\nabla_x T + L_{13}\nabla_y T. \quad (6.10.12d)$$

Equation (6.10.12b) shows that the establishment of a longitudinal temperature gradient gives rise to a transverse one. This interrelation is known as the *Righi–Leduc effect*. It is convenient to rewrite Eq. (6.10.12b) as

$$\nabla_y T = (L_{12}/L_{11}\mathcal{H}_z)\mathcal{H}_z\nabla_x T, \quad (6.10.13a)$$

whence the Righi–Leduc coefficient becomes

$$\nabla_y T/\mathcal{H}_z\nabla_x T \equiv \mathcal{M} = L_{12}/L_{11}\mathcal{H}_z. \quad (6.10.13b)$$

Another relation of interest is found by inserting Eq. (6.10.13a) into Eq. (6.10.12a), and multiplying through by T ; this yields

$$J_s^x T = -T(L_{11} + L_{12}^2/L_{11})\nabla_x T, \quad (6.10.14a)$$

which gives rise to the definition for the *adiabatic thermal conductivity*.

$$\kappa_A = T(L_{11} + L_{12}^2/L_{11}). \quad (6.10.14b)$$

Use of Eq. (6.10.13a) in Eq. (6.10.12c) yields

$$\nabla_x(\zeta/e) = (L_{12} + L_{14}L_{12}/L_{11})\nabla_x T, \quad (6.10.15a)$$

which is the *Seebeck effect* when adiabatic conditions are maintained in the transverse direction. The corresponding *coefficient* reads

$$\alpha_A = L_{13} + L_{14}L_{12}/L_{11}. \quad (6.10.15b)$$

Finally, if Eq. (6.10.13a) is combined with Eq. (6.10.12d) and the magnetic field is explicitly introduced, one finds

$$\nabla_y(\zeta/e) = (1/\mathcal{H}_z)(-L_{14} + L_{13}L_{12}/L_{11})\mathcal{H}_z\nabla_x T, \quad (6.10.16a)$$

which leads to the *adiabatic transverse Nernst effect*, with a corresponding *coefficient* of the form

$$\mathcal{N}_A = (1/\mathcal{H}_z)(-L_{14} + L_{13}L_{12}/L_{11}). \quad (6.10.16b)$$

Many more effects may be treated on an analogous basis, as is suggested by Exercises 6.10.1 and 6.10.2. The physical basis on which these effects rest is to be explored in Exercise 6.10.3.

One should note that the various coefficients listed in this section are all measurable experimentally according to the prescriptions imposed by the boundary conditions (a)–(d) and the indicated definitions for each coefficient. Also, having set up phenomenological equations in partially inverted form, the phenomenological coefficients L_{jj} in Eqs. (6.10.1) assume a particularly simple form:

$$L_{11} = \kappa_I T, \quad (6.10.17a)$$

$$L_{12} = -\mathcal{H}_z \kappa_I \mathcal{M}/T, \quad (6.10.17b)$$

$$L_{13} = \alpha_I, \quad (6.10.17c)$$

$$L_{14} = -\mathcal{H}_z \mathcal{N}_I, \quad (6.10.17d)$$

$$L_{33} = \rho_I, \quad (6.10.17e)$$

$$L_{34} = -\mathcal{H}_z \mathcal{R}_I. \quad (6.10.17f)$$

On inserting these relations into Eqs. (6.10.1), one thus obtains a complete description of irreversible processes for the system under study. This in turn, permits an analysis to be made of the 560 possible galvanothermomagnetic effects that can be achieved in the rectangular parallelepiped geometry of Figure 6.10.1.

Exercises

- 6.10.1.** Develop phenomenological relations for the set of conditions $\mathcal{J}_x = \nabla_y T = \mathcal{J}_s^x = 0$, and prove that a temperature gradient is set up along x as a consequence of current flow along that direction. What is the resultant heat flux along y ? Express the resistivity and Hall coefficients in terms of the various L_{ij} .
- 6.10.2.** Impose the conditions $\mathcal{J}_x = \mathcal{J}_s^x = 0$ on the phenomenological equations. Express $\nabla_x T$ and $\nabla_{xy} T$ in terms of \mathcal{J} . Express the resistivity and Hall coefficient in terms of appropriate L_{ij} and compare your results to those in the text.
- 6.10.3.** Provide physical mechanisms that show how transverse interference effects arise under the various boundary conditions that were taken up in the text.
- 6.10.4.** Express the ratio of adiabatic to isothermal transport coefficients in terms of the various L_{ij}

7.0 Introductory Remarks

In this chapter, we provide a heuristic introduction to scaling procedures that characterize the properties of systems close to their critical point. The objective is to provide some general insights and to convey the flavor of the methodology. Much of the treatment of critical phenomena depends on advanced mathematical techniques beyond our purview. However, certain illuminating aspects can be discussed without the use of these techniques. We center the discussion on critical exponents and the Landau theory of critical phenomena. For a more extensive exposition of the subject, the reader is referred to several sources in the literature¹.

7.1 Properties of Materials Near Their Critical Point

Scaling Procedures

The problems arising in the thermodynamic approach to critical phenomena were briefly mentioned in Section 2.3, in connection with the van der Waals equation of state. Problems arise because all standard thermodynamic treatments involve an averaging procedure: a given molecule moves in and interacts with the field derived from all the other materials in the system. The correct treatment of this problem leads to intractable mathematics. In its place, thermodynamics relies on a *mean field* systematization of experimental observations. Normally this works well for macroscopic systems—witness all the materials in the preceding chapters. However, as we will shortly show, near the critical point any system displays large-scale fluctuations. These affect physical properties of the material that cannot be quantitatively characterized by standard methods. Hence the need for a new approach that comes under the heading of *scaling laws*.

Scaling procedures are prompted by the failure of commonly used functions of state to deal with materials close to criticality. Consider again the theoretical *Drosophila* for fluids,² the van der Waals equation of state. As shown in Section 2.3, in its reduced formulation, the equation of state reads

$$(\pi + 3/v^2)(3v-1) = 8\tau, \quad (7.1.1)$$

where $\pi \equiv P/P_c$, $v \equiv V/V_c$, $\tau \equiv T/T_c$, where the subscript denotes the values of the control parameters at the critical point. No reference is made to any materials properties; so, Eq. (7.1.1) could be expected to apply any fluid. Such a relation is termed the *Law of Corresponding States*. Similarly, the *compressibility ratio* $Z \equiv PV/RT = 3/8$ for a van der Waals fluid is a universal constant.

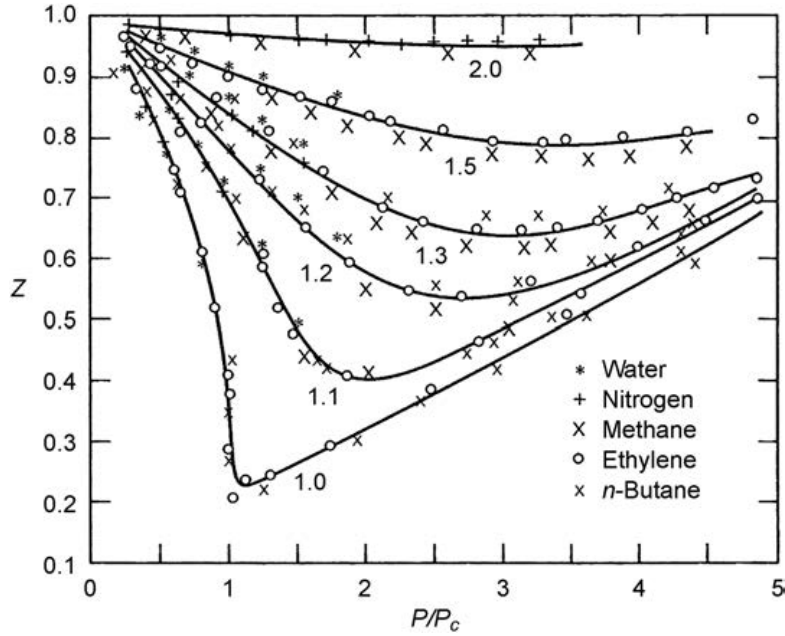


FIGURE 7.1.1

Plot of the compressibility Z for five different fluids against reduced pressure P/P_c at a series of reduced temperatures T/T_c , as indicated by the numerical figures next to each graph. Note the remarkable superposition of the data points and the significant deviation of the actual curves from the ideal gas law $Z = 1$. Reproduced from R.S. Berry, S.A. Rice, J. Ross, *Physical Chemistry*, 2nd Ed., Oxford University Press, 2000; used by permission of Oxford University Press, USA.

The extent to which real fluids obey the van der Waals equation of state is shown in Figure 7.1.1, in terms of the dependence of the ratio Z on reduced pressure at different reduced temperatures for five different systems near their respective critical points. Obviously a certain universality scaling law is well obeyed at each T/T_c , but the observed numerical values for Z differ greatly from the above prediction; hence, the need for a different approach that leads to a theory in agreement with experiment.

For the second illustration of the quantitative failure of the van der Waals equation close to criticality, consider small deviations $t \equiv \tau - 1 = (T - T_c)/T_c$ and $\phi \equiv v - 1 = (V - V_c)/V_c$ from the critical point, at which $\pi = \tau = v = 1$. In terms of these parameters, the reduced equation of state then becomes

$$\pi = \frac{8(1+t)}{3(1+\phi)-1} - \frac{3}{(1+\phi)^2}, \quad (7.1.2)$$

which, near the critical point may be expanded as

$$\pi = 1 + 4t - 6\phi t - 3\phi^3/2 + 9\phi^2 t + 27\phi^3 t/2. \quad (7.1.3)$$

We may discard the last two terms. The reduced coexistence volumes $v_l(P)$ and $v_g(P)$ for the liquid and vapor phase, respectively, are in equilibrium at $T < T_c$; equivalently, so are the corresponding quantities ϕ_l and ϕ_g . We now relate the properties of the liquid and vapor phases: with reference to Figure 7.1.2 (where, however, the pressure vs volume is plotted in a highly schematic manner for

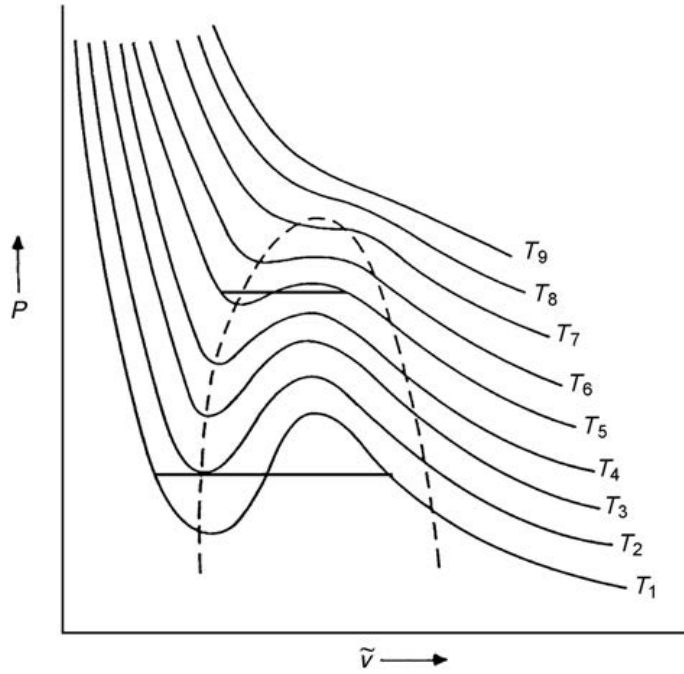


FIGURE 7.1.2

Schematic diagram for the pressure–volume relationship for a van der Waals fluid at a series of temperatures. The Maxwell equal area rule applies in each case.

purely illustrative purposes), we apply Maxwell’s equal area rule to require that, for a fixed value of $t < 0$, $\int_{P_l}^{P_g} V dP = 0 = V_c \int_{P_l}^{P_g} (V/V_c - 1) dP \equiv I$. Because $\int P_g dP = 0$ over the horizontal path indicated in the figure, the entire integral I vanishes as well. But by Eq. (7.1.3), we find that $dP = -P_c(6t + 9\phi^2/2)d\phi$, whence I may be reformulated as

$$\int_{\phi_l}^{\phi_g} P_c \phi [6t + 9\phi^2/2] d\phi = 0. \quad (7.1.4a)$$

This equation must be satisfied for all fixed t for which the approximation (7.1.3) holds. On integrating we are led to the requirement

$$3t(\phi_g^2 - \phi_l^2) + (9/8)(\phi_g^4 - \phi_l^4) = 0, \quad (7.1.4b)$$

which is met by setting $\phi_g = \pm \phi_l$. We discard the positive root which leads to an identity. On applying the condition $\phi_g = -\phi_l$ to Eq. (7.1.3), we obtain

$$\pi_g = 1 + 4t - 6t\phi_g - 3\phi_g^3/2; \quad \pi_l = 1 + 4t + 6t\phi_g + 3\phi_g^3/2. \quad (7.1.5)$$

When we subtract, adopt $\pi_g = \pi_l$ and solve for ϕ_g , we predict that either $\phi_g = 0$ or

$$\phi_g = 2\sqrt{(-t)} \sim [(T_c - T)/T_c]^{1/2} \quad (T < T_c; t < 0) \quad (7.1.6)$$

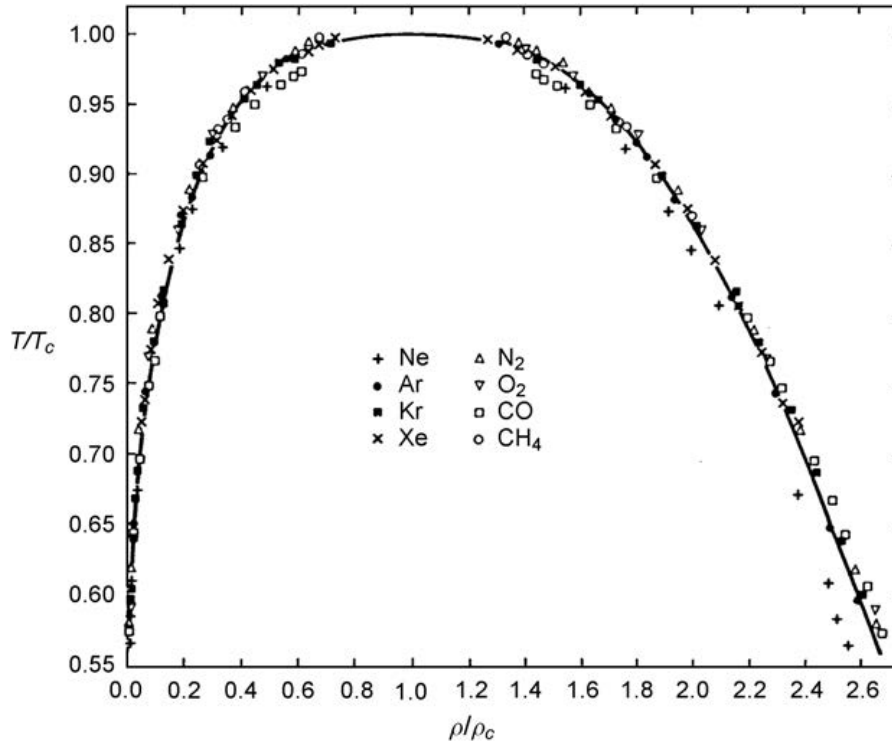


FIGURE 7.1.3

Data near the critical point of eight fluids involving the reduced temperature T/T_c plotted against the reduced density ρ/ρ_c . Note the remarkable superposition of the data points.

showing that the reduced volume should change as the square root of the small deviation of T from its critical value. This is in serious disagreement with experimental observation: Figure 7.1.3 shows a plot of reduced temperature vs reduced density for eight distinct fluids.³ The collapse of virtually all these data onto a single curve is striking. However, while all these data fall on a single curve, the corresponding critical exponent is close to $\beta \approx 1/3$, rather different from the value $1/2$ cited in Eq. (7.1.6). Measurements on many other systems have shown that in general $\varphi \sim (-t)\beta$, with β in the range 0.31–0.33.

Similarly, at $T = T_c$, $t = 0$, Eq. (7.1.3) leads to the following result,

$$\pi - 1 = (P - P_c)/P_c = -3[(V - V_c)/V_c]^3/2, \quad (7.1.7)$$

which also disagrees with observation: experimentally the reduced pressure varies with reduced volume as φ^δ , with δ in the range 4.6–4.9. These findings again reflect the fact that the van der Waals equation of state has been applied to a range where mean field theory is inadequate, because fluctuations dominate. Therefore, some other method for characterizing critical phenomena in fluids must be found.

Many other physical phenomena are subject to similar problems. Among the most commonly treated of these is the ferromagnet. Figure 7.1.4 shows how the magnetization of nickel changes with rising temperature.⁴ The initially gradual falloff accelerates as a critical temperature T_c is approached, beyond which the material remains essentially unmagnetized. Remarkably, variations of magnetization M near

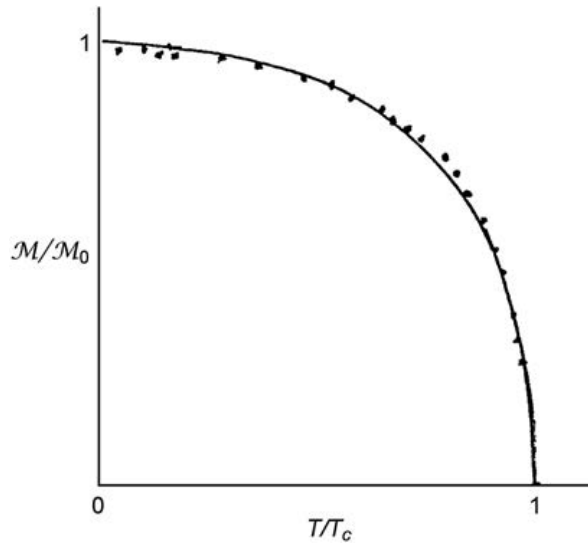


FIGURE 7.1.4

Dependence of the reduced magnetization $\mathcal{M}/\mathcal{M}_0$ on reduced temperature T/T_c for Ni metal. The solid points indicate experimental measurements. The reduced magnetization represents an order parameter of unity at $T = 0$ and of zero at the critical temperature T_c .

the critical temperature follow the same power law dependence on temperature as the density measurements for fluids, namely: $M \sim |T - T_c|^\beta$, with exponents again in the range ≈ 0.33 .

This similarity in characteristics may be understood as follows: the elemental units in a fluid are the constituent atoms, while those of the ferromagnet are the electron spins residing on lattice sites. As the critical point is approached from above, magnetized domains with perfect spin alignments grow as islands within the unmagnetized matrix, and their size ultimately becomes very large compared to the atomic dimensions. Similarly, as the critical temperature of a fluid is approached from above, liquid droplets of increasing size begin to float in the vapor phase and ultimately combine to form a larger liquid phase. Hence, one may heuristically point to the analogy between magnetization and liquid–gas transitions near the critical point. The domains of perfect spin alignment or liquid droplet sizes are much larger than atomic dimensions, whence the atomic constitution of the phase is no longer relevant. However, one must grapple with the fact that the mean field theory leads to an incorrect specification of the critical exponent for magnetization. A different approach is called for.

Thermodynamic Properties near the Critical Point

Preliminary to such a search we examine several thermodynamic properties of fluids at or close to criticality that clearly show why and how fluctuations dominate under such conditions. (1) Consider first the isothermal compressibility, $\kappa_I = -(\partial V/\partial P)_T/V$. At the critical point the isotherm $(\partial P/\partial V)_T$ has zero slope; thus, κ_I grows indefinitely as $T \rightarrow T_c$. (2) Using Eq. (1.3.8) and the definition for κ_I one finds that $(\partial V/\partial T)_P = -(\partial V/\partial P)_T (\partial P/\partial T)_V = \kappa_I V (\partial P/\partial T)_V$, wherein $(\partial P/\partial T)_V$ does not vanish. Therefore, the coefficient of thermal expansion, $\beta_T = (1/V)(\partial V/\partial T)_P$ also grows without limit as the critical point is approached. (3) According to the Clausius–Clapeyron equation, rewritten in the form

$\Delta H = T(V_g - V_l)(dP/dT)$, the heat of vaporization of the fluid near the critical point becomes very small, since $V_g - V_l \rightarrow 0$, whereas dP/dT remains finite.

Thus, in circumstances peculiar to criticality, just below T_c the liquid state becomes highly compressible, and can readily be converted to the vapor with expenditure of very little enthalpy. This, in turn, produces significant fluctuations in the density and related properties of liquid and gas. Since the overall density of the closed system is fixed at any particular temperature, small regions of high density must be compensated for by small regions of lower than average density. These large-scale variations, which attest to the growing indistinguishability between liquid and vapor near the critical point, are ignored in the thermodynamic mean field theory. Analogous remarks apply to magnetized domains forming in an unmagnetized background near the critical point.

The peculiar properties cited above are reflected by a review of the following experimental findings:

1. Near the critical point, the densities of the liquid and gas converge toward each other according to the relation

$$|\rho_l - \rho_g| \sim |T_c - T|^\beta, \quad \beta = 0.326 \pm 0.002, \quad (7.1.8)$$

where the experimentally determined quantity β is termed a *critical exponent*.

2. The difference in chemical potential near criticality is specified by

$$\mu - \mu_c \sim |\rho - \rho_c|^{\delta-1}(\rho - \rho_c), \quad \delta = 4.80 \pm 0.02. \quad (7.1.9)$$

3. The heat capacity at constant volume obeys the relation

$$C_V \sim |T - T_c|^{-\alpha}, \quad \alpha = 0.110 \pm 0.003, \quad (7.1.10)$$

which explicitly shows the power law divergence of the heat capacity at the critical point.

4. The isothermal compressibility for a wide variety of substances obeys the following relation:

$$M^{-1}(\partial\mu/\partial\rho)_T = \rho^{-2}\kappa_T \sim |T - T_c|^{-\gamma}, \quad \gamma = 1.239 \pm 0.002, \quad (7.1.11a)$$

where M is the gram molecular mass.⁵ This again shows the power law divergence of κ_T . Equivalently, for the pressure–volume dependence, we may write

$$(P - P_c) \sim |V - V_c|^{\delta-1}(V_c - V). \quad (7.1.11b)$$

The truly remarkable feature is that the values of the various critical exponents are universal, i.e., independent of the chemical constitution of materials near their respective critical points. As already stated, for fluids, this feature arises because the range of fluctuations in properties such as density greatly exceeds atomic dimensions.

The Ising Model and Its Characteristics

The Ising Model and Hamiltonian

Up to this point, we have studied the properties of fluids and gases near their respective critical points. We now show very similar results prevail for localized models, as represented by the so-called Ising (pr. Eezing) model. This involves a set of elementary atomic spins placed on a regularly spaced two-dimensional lattice point array of N elementary constituents, immersed in a magnetic field \mathcal{B} , that is

oriented in the perpendicular direction. Each lattice component displays a magnetic dipole, associated “spin” of which is specified by $S_i = \pm S$ ($i=1,2,\dots,N$). Thus the spins are aligned with or against the applied field with energy $-\mu S\mathcal{B}$.

The Hamiltonian \mathcal{H} for such a configuration is specified by

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} S_i S_j - \sum_i \mu S_i \mathcal{B}, \quad (7.1.12)$$

where μS_i is the magnetic moment associated with site i , J is a positive coupling constant for interactions between nearest neighbors, and the symbol $\langle i,j \rangle$ restricts the summation to nearest neighbor sites; longer range interactions are ignored. We seek to investigate the critical properties of this elementary system.

Further approximations are introduced at this point. We apply the identity $S_i \equiv \langle S_i \rangle + (S_i - \langle S_i \rangle)$ where angular brackets signify expectation values. Also, $\langle S_i \rangle \equiv \mathcal{M}$ represents the average magnetization. We next set $(S_i - \langle S_i \rangle) \equiv \delta S_i$ as the (presumably small) fluctuating instantaneous deviations of the local spin from its average value. Since $S_i \equiv \mathcal{M} + (S_i - \mathcal{M})$, we rewrite the Hamiltonian in the form of

$$\begin{aligned} \mathcal{H} &= -J \sum_{i,j} [\mathcal{M} + (S_i - \mathcal{M})][\mathcal{M} + (S_j - \mathcal{M})] - \sum_i S_i \mu \mathcal{B}, \\ &= -J \sum_{i,j} \{ \mathcal{M}^2 + \mathcal{M}(S_i - \mathcal{M}) + \mathcal{M}(S_j - \mathcal{M}) + \delta S_i \delta S_j \} - \sum_i S_i \mu \mathcal{B}, \\ &= -J \sum_i (z \mathcal{M} S_i - z \mathcal{M}^2 / 2) - \sum_i S_i \mu \mathcal{B}, \end{aligned} \quad (7.1.13)$$

where in the last line, we neglected the square of the local spin deviations and introduced z as the number of the nearest neighbors in the square planar array. Neglecting edge effects, this restricts the summation to the $Nz/2$ bonds in the plane. The neglect of the spin fluctuations immediately consigns the theory to an equilibrium configuration status.

The Ising Partition Function and Free Energy

For further progress, we sum the N identical contributions involving \mathcal{M}^2 and introduce an effective field as $\mathcal{B}_{\text{eff}} \equiv Jz\mathcal{M} + \mu\mathcal{B}$, whereby the Hamiltonian assumes the form

$$\mathcal{H} = NJz\mathcal{M}^2/2 + \sum_i S_i \mu \mathcal{B}_{\text{eff}}. \quad (7.1.14)$$

On setting $S_i = \pm S$, the partition function for the system reads ($\beta \equiv 1/k_B T$)

$$\mathcal{Z} = e^{-\beta \mathcal{H}} = e^{-\beta NJz\mathcal{M}^2/2} (e^{\beta S \mathcal{B}_{\text{eff}}} + e^{-\beta S \mathcal{B}_{\text{eff}}})^N = e^{-\beta NJz\mathcal{M}^2/2} \{2 \cosh \beta S \mathcal{B}_{\text{eff}}\}^N. \quad (7.1.15)$$

The free energy associated with the magnetic properties is derived from $F_m = -k_B T \ln \mathcal{Z}$ we find that

$$F_m = F_m(T, \mathcal{B}_{\text{eff}}, \mathcal{M}) = NJz\mathcal{M}^2/2 - Nk_B T \ln (2 \cosh \beta S \mathcal{B}_{\text{eff}}). \quad (7.1.16)$$

The Regime Close to Criticality

In what follows, we specialize to the regime close to the critical point where the long-range magnetization order almost disappears. This allows us to introduce a parameter $u \equiv \beta Jz\mathcal{M}S$ and to expand the hyperbolic function as an ascending power series up to u^4 , which restricts us to small departures from $u = 0$.

We further consider the case of the field-free region, $\mathcal{B} = 0$ and combine the $\ln 2$ factor on the right of Eq. (7.1.16) with the free energy portion that excludes the magnetic contributions. The expansion of $\cosh u$ to fourth order terms reads

$$\cosh u = 1 + u^2/2! + u^4/4!. \quad (7.1.17)$$

The logarithmic expansion to fourth order has the form

$$\ln \cosh u = \ln[1 + (u^2/2)(1+u^2/12)] \approx (u^2/2)(1+u^2/12) - u^2/8 = u^2/2 - u^4/12. \quad (7.1.18)$$

We then find that

$$F_u \approx F_0(T) + \frac{NJ_z \mathcal{M}^2}{2} - Nk_B T \left\{ \frac{u^2}{2} - \frac{u^4}{12} \right\}. \quad (7.1.19)$$

Since $J_z S^2$ has the dimension of energy, we may associate this product with an equivalent temperature $k_B T_u \equiv J_z S^2$, which simplifies the subsequent analysis.

Now examine the terms in Eq. (7.1.19) involving the factor $1/2$

$$F_2 \equiv NJ_z \mathcal{M}^2/2 - Nk_B T (\beta J_z \mathcal{M} S)^2/2, \quad (7.1.20)$$

and introduce T_u to find

$$F_2 = NJ_z \mathcal{M}^2/2 - Nk_B T (T_u/T S)^2 \mathcal{M}^2/2. \quad (7.1.21)$$

Proceed in analogous fashion with the quartic term in Eq. (7.1.19). On combining the results, we arrive at the fundamental relationship

$$F_u(\mathcal{M}; T, J, z, S) \approx F_0 + NJ_z S^2 \left[\left(1 - \frac{T_u}{T} \right) \frac{\mathcal{M}^2}{2S^2} + \left(\frac{T_u}{T} \right)^3 \frac{\mathcal{M}^4}{12S^4} \right]. \quad (7.1.22)$$

This features \mathcal{M}/S as the relevant independent variable and contains several experimental parameters, including the temperature T . F_u has the form of a free energy function but is not the thermodynamic free energy because it has not been subjected to equilibrium constraints that are introduced next.

The examination of Eq. (7.1.22), divided into three parts, is instructive: when $T > T_u$, both terms in the square brackets are positive so that $F_u - F_0$ rises with \mathcal{M}/S from zero, as sketched in the top curve of Figure 7.1.5. Precisely at the critical temperature $T = T_u$, the free energy density varies as \mathcal{M}^4/S^4 , emerging from zero as the flattened curve depicted in the middle. This invites the observation that large excursions in magnetizations from the mean are anticipated. When $T < T_u$, the first term in brackets is negative; initially, $F_u - F_0$ decreases with rising $|\mathcal{M}/S|$, but the positive contribution from \mathcal{M}^4/S^4 ultimately outweighs the negative factor, giving rise to the bottom curve in Figure 7.1.5. Now the minimum of the free energy no longer occurs at $\mathcal{M}/S = 0$, but at the minima $(\mathcal{M}/S)_0$.

Equilibrium Constraints

At this point, we introduce the equilibrium constraint on the function (7.1.16). Setting $\partial F_u / \partial \mathcal{M} = 0$ leads to the self-consistency relation

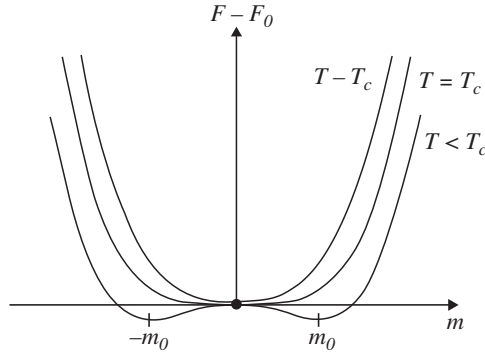


FIGURE 7.1.5

Sketch of the free energy function (7.1.22) as a function of M/S . Top Curve: $T > T_c$; Middle Curve: $T = T_c$; Bottom Curve: $T < T_c$.

$$\mathfrak{M} = S \tanh u = S \tanh(\beta J_z S \mathfrak{M}), \quad (7.1.23)$$

This relation clearly shows that \mathfrak{M} and β (i.e., T) now are no longer independent variables. In our present approximation scheme, the hyperbolic function (7.1.23) assumes the form $\tanh u = u - u^3/3$ so that

$$\mathfrak{M} = \beta J_z S^2 \mathfrak{M} - \left(\frac{1}{3}\right) (\beta J_z)^3 S^4 \mathfrak{M}^3, \quad (7.1.24)$$

where

$$1 = \beta J_z S^2 - \left(\frac{1}{3}\right) \left[(\beta J_z S^2)^3 \mathfrak{M}^2 / S^2 \right], \quad (7.1.25)$$

which is rewritten in the form of

$$\frac{\mathfrak{M}}{S} = \pm \left[3 \frac{1 - \beta J_z S^2}{(\beta J_z)^3 S^6} \right]^{1/2}. \quad (7.1.26)$$

Of special interest is the ferromagnet precisely at the critical temperature, where $T = T_u \equiv T_c$, $\mathfrak{M} = 0$. Then

$$k_B T_c = J_z S^2. \quad (7.1.27)$$

We have thereby identified T_u with T_c when equilibrium prevails; moreover, in the neighborhood of $\mathfrak{M} = 0$, T does not differ substantially from T_c . Note further than Eq. (7.1.26) does not admit of a physically acceptable solution for \mathfrak{M}/S when $T > T_c$.

Specialization

When interest centers on phenomena in the immediate vicinity of the critical point, it is customary to introduce two approximations in handling Eq. (7.1.22): the distinction between T and T_c in the quartic term $(\mathfrak{M}/S)^4$ is ignored; the corresponding multiplier is dropped. Also, on introducing the definition $t \equiv (T - T_c)/T_c \ll 1$, the multiplier of $\mathfrak{M}^2/2S^2$ may be rewritten as

$$1 - \frac{T_c}{T} = 1 - \frac{1}{1+t} \approx t = \frac{T}{T_c} - 1. \quad (7.1.28)$$

In that case, close to the critical temperature, we end up

$$F(T; T_c, J, z, S) \approx F_0 + NJzS^2 \left[\left(\frac{T}{T_c} - 1 \right) \frac{\mathcal{M}^2(T)}{2S^2} + \frac{\mathcal{M}^4(T)}{12S^4} \right], \quad (7.1.29)$$

which is the basic relation of interest. In the current approximation the thermodynamic free energy density involves solely T as the independent variable; the remaining quantities are parameters appropriate to the model under study.

Elementary Consequences of the Model

We can finally explore some physical consequences: in what follows, we consider the special case $S = 1$, which somewhat lightens the notation.

1. Consider first the spontaneous magnetization at $T < T_c$ in the absence of a magnetic field. Referring back to Eq. (7.1.27), rewrite Eq. (7.1.25) as

$$1 = \frac{T_c}{T} - \frac{1}{3} \left(\frac{T_c}{T} \right)^3 \mathcal{M}^2. \quad (7.1.30)$$

On again introducing the dimensionless quantity $t \equiv T/T_c - 1$, to first order in t Eq. (7.1.30) reads

$$\mathcal{M} = \left[-3 \left(\frac{T}{T_c} \right)^3 t \right]^{1/2} = \left[-3 (1+t)^3 t \right]^{1/2} \approx \sqrt{-3t} \approx \sqrt{3(T_c - T)}, \quad (T < T_c). \quad (7.1.31)$$

Note several points: Close to T_c , we neglected terms in t^2 or higher powers. Also, in the absence of an external magnetic field, \mathcal{M} is defined only for $T < T_c$. Then, the magnetization varies as the square root with deviations from the critical point when approached from next.

Of great interest is the fact that we have seen this type of relationship before. In Eq. (7.1.6), we showed that the mechanical equivalent of the magnetization, namely, the deviation of the fluid volume from its critical value, $(\varphi)_g$, varies as $\sqrt{3(T_c - T)}$, ($T < T_c$). That two completely different models of reality exhibit exactly the same temperature dependence close to criticality at vastly different T_c values are striking. This can only mean that differences in atomic properties become irrelevant near the critical regime. In Section 7.1, we cited experimental verifications of other types of universality properties.

This universality principle is also encountered in far more sophisticated theories of critical phenomena. However, the exact theories indicate that the magnetization near the critical temperature goes to zero as $(T_c - T)^\beta$, with β very close to the experimentally observed $\beta = 0.326 \pm 0.002$ (not to be confused with $1/k_B T$). The difference with the mean-field value of $\beta = 1/2$ may seem to be very small, but it is precisely discrepancies of this magnitude that led to an enormous effort to construct a better theory, based on fluctuations that were neglected in mean-field theory.

2. Of interest also is the magnetization in a weak external magnetic field at temperatures close to the critical value. Generalize Eq. (7.1.23) to read $\mathcal{M} = \tanh(\beta Jz\mathcal{M} + \beta\mu\mathcal{B})$ and retain only the

first-order term. Then, (a) for $T > T_c$, where the magnetization arises solely from the existence of the field,

$$\mathcal{M} = \beta J_z \mathcal{M} + \beta \mu \mathcal{B} = \left(\frac{T_c}{T} \right) \mathcal{M} + \beta \mu \mathcal{B}, \quad (7.1.32)$$

which may be solved for

$$\mathcal{M} = \frac{\mu \mathcal{B}}{(1 - T_c/T) k_B T} = \frac{\mu \mathcal{B}}{k_B (T - T_c)}, \quad (7.1.33)$$

showing that in weak externally applied magnetic fields, the magnetization diverges as the critical temperature is approached from the above. The magnetic susceptibility χ_T involves the total magnetization of the system, $N\mu\mathcal{M}$, where

$$\chi_T = \left(\frac{\partial N\mu^2 \mathcal{B}}{\partial \mathcal{B}} \right)_{\mathcal{B} \rightarrow 0} = \frac{N\mu^2}{k_B (T - T_c)}. \quad (7.1.34)$$

Below the critical temperature, we must include the additive effect of the spontaneous magnetization. We assume that the result should not deviate significantly from the above magnetization $\mathcal{M}_0 = \sqrt{-3t}$ so that we may write

$$\mathcal{M} = \mathcal{M}_0 + e, \quad (7.1.35)$$

where e is a small quantity. The subsequent operation is simplified by adapting Eq. (7.1.23) to read $\mathcal{M} = \tanh(\beta J_z \mathcal{M} + \beta \mu \mathcal{B})$, and then carrying out the inverse operation

$$\tanh^{-1} \mathcal{M} = \beta J_z \mathcal{M} + \beta \mu \mathcal{B} = \mathcal{M} + (1/3)\mathcal{M}^3, \quad (7.1.36)$$

where we have retained only the first two terms in the expansion of the left. Now introduce Eq. (7.1.27) to rewrite the above as

$$\left(\frac{T_c}{T} - 1 \right) \mathcal{M} = \frac{1}{3} \mathcal{M}^3 - \frac{\mu \mathcal{B}}{k_B T}. \quad (7.1.37)$$

As shown in the appendix, on introducing appropriate approximations and using Eq. (7.1.13), with $\mathcal{M}_0^2 = -3t$, one ends up with

$$e = \frac{-\mu \mathcal{B}}{2k_B (T - T_c)}, \quad (7.1.38)$$

where the magnetic susceptibility is given by

$$\chi_T = \left(\frac{\partial N\mu e}{\partial \mathcal{B}} \right)_{\mathcal{B} \rightarrow 0} = \frac{N\mu^2}{2k_B (T_c - T)} \sim (T_c - T)^{-1}. \quad (7.1.39)$$

Thus we encounter the same divergent power law as in case (a) but differing in sign and by a numerical factor of 1/2.

3. Of additional interest is the dependence of the magnetization on the applied magnetic field exactly at the critical temperature. Return to Eq. (7.1.36) and set $T = T_c$, where

$$\mathcal{M} = \mathcal{M} + (1/3)\mathcal{M}^3 - \mu\mathcal{B}/k_B T_c, \quad (7.1.40)$$

or

$$\mathcal{B} = \left(\frac{k_B T_c}{3\mu} \right) \mathcal{M}^3, \quad (7.1.41)$$

so that the magnetization at $T = T_c$ obeys the proportionality $\mathcal{M} \sim \mathcal{B}^{1/3}$.

4. Finally, we investigate the heat capacity in the absence of an applied field as we pass the critical temperature. Just below T_c , the magnetic contribution to the internal energy is given by

$$\mathcal{E}_m = -\frac{NJz}{2}\mathcal{M}_0^2 \approx -\frac{3}{2}NJz\left(\frac{T_c - T}{T_c}\right) = \frac{3}{2}Nk_B(T - T_c), \quad (7.1.42)$$

where the heat capacity just below T_c is specified by

$$\mathcal{C} = 3Nk_B/2. \quad (7.1.43)$$

Above T_c , $\mathcal{E}_m = \mathcal{C} = 0$; hence, in the Ising model the heat capacity exhibits a discontinuity on crossing the critical temperature.

Discussion

It is rather impressive how many physical predictions can be based on such a rudimentary model as the Ising lattice. However, one cannot expect the abovementioned theory to provide an accurate interpretation of experimental observations. An important reason for the failure of the primitive model is our neglect of the fluctuations δS_i in Eq. (7.1.13); every spin S_i has been replaced by its average value S , a procedure that is known as the *mean-field approximation*. Also, the only allowed configuration is one in which the spins are in alignment with or against a magnetic field, however, weak. To conform more closely to reality, one should adopt the Heisenberg model in which each spin is represented as a vector, the specification of which requires not only the magnitude but also the relative orientations of the spins. Thus at best, we have achieved a highly approximate phenomenological theory to deal with the experimental observations in real-life situations.

A preliminary comparison may be instructive: for dealing with experimental results, the following standard notation has been in use. At or close to the critical temperature, the heat capacity is specified by

$$\mathcal{C} \sim |T - T_c|^{-\alpha}, \quad (7.1.44)$$

the average spin (or magnetization) is specified by

$$\mathcal{M}_0 \sim (T_c - T)^\beta, T < T_c, \quad (7.1.45)$$

the magnetic susceptibility is specified by

$$\chi_T \sim |T - T_c|^{-\gamma}, \quad (7.1.46)$$

the relation between the applied magnetic field and the average spin (or magnetization) is specified by

$$\mathcal{B} \sim \mathcal{M}^\delta, T = T_c. \quad (7.1.47)$$

The abovementioned four exponents listed are known as *critical indices* or *critical exponents*.

It is of interest to compare the abovementioned exponents with those obtained by an analysis in two dimensions ($d = 2$) and with numerical calculations in three dimensions ($d = 3$).

	Mean field	$d = 2$	$d = 3$	Observed average
α	discontinuous	$\ln T - T_c $	0.110	0.110
β	0.5	0.125	0.312	0.326
γ	1	1.75	1.238	1.239
δ	3	15	5.0	4.80

The uncertainties in numerical values are in the next digits. The table uncovers striking variations: aside from numerical differences, the mean-field values do not depend on the dimensionality of the system, whereas the sophisticated calculations do.

Appendix

Use Eq. (7.1.37); define $q \equiv ((T_c/T) - 1)$, set $\mathfrak{M} = \mathfrak{M}_0 + e$, with $\mathfrak{M}_0^2 = -3t$, $t \equiv (T/T_c) - 1$. Then Eq. (7.1.37) reads

$$q(\mathfrak{M}_0 + e) = \left(\frac{1}{3}\right)(\mathfrak{M}_0 + e)^3 - \frac{\mu\mathcal{B}}{k_B T} \approx \left(\frac{1}{3}\right)\mathfrak{M}_0^2(\mathfrak{M}_0 + 3e) - \frac{\mu\mathcal{B}}{k_B T}, \quad (7.1.48)$$

where in the cubic expansion, we discard terms in e^2 and e^3 as being of higher order. Then

$$\mathfrak{M}_0 + e = \frac{1}{3} \left(-3 \frac{t}{q} \right) (\mathfrak{M}_0 + 3e) - \frac{\mu\mathcal{B}}{k_B T q} = \left(1 + t \right) (\mathfrak{M}_0 + 3e) - \frac{\mu\mathcal{B}}{k_B T q}. \quad (7.1.49)$$

We neglect the term in t , since t multiplies a term of first order. Eq. (7.1.38) now follows.

Notes and References

- 7.1.1.** N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group* (Perseus Books, Reading, MA 1992). H.E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, London, 1971). S. Ma, *Modern Theory of Critical Phenomena* (W.A. Benjamin, Reading, MA, 1976). J.J. Binney, N.J. Dowrick, A.J. Fisher, M. E. J. Newman, *The Theory of Critical Phenomena* (Clarendon Press, Oxford, 2002). J. Zinn-Justin, *Quantum Field Theory and Critical Phenomena* (Oxford University Press, Oxford, 1989).
- 7.1.2.** I have adopted this characterization as a direct quote from N. Goldenfeld, loc. cit.
- 7.1.3.** E.A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945).
- 7.1.4.** P. Weiss and R. Forrer, *Ann. de Physique* **15**, 153 (1926).
- 7.1.5.** This relationship is established as follows ($v \equiv V/n$):

$$\begin{aligned} (\partial\mu/\partial\rho)_T &= (M/\rho)(\partial p/\partial\rho)_T = (M/\rho)(\partial p/\partial v)_T (\partial v/\partial\rho)_T = -(M^2/\rho^3)(\partial p/\partial v)_T \\ &= -(v^2/\rho)(\partial p/\partial v)_T = -(v^2/M)v(\partial p/\partial v)_T \equiv (M/\rho^2)\kappa_I = (v^2/M)\kappa_I. \end{aligned}$$

7.2 Homogeneity Requirements, Correlation Lengths, and Scaling Properties

Because of the failure of the van der Waals equation of state near the critical point, we look for a different characterization of fluids in that regime. With diminishing T close to T_c droplets of liquid begin to form in the vapor, there is obviously a distribution of droplet “sizes,” but one can determine an average “diameter” ξ , known as a *correlation length*, that characterizes the physical extension of the droplet floating in the vapor. It also specifies the range over which fluctuations in physical properties tend to be uniform. This macroscopic quantity is expected to depend on the experimental conditions and to grow without limit as the critical temperature is approached from the above. Since the homogeneous regions of materials near criticality become very large compared to atomic size, critical phenomena should be independent of the microscopic characteristics of the system. To deal with such a situation, we introduce next the concept of *scale invariance*. This concept is verified experimentally by the features such as the collapse of all data onto a single curve in Figure 7.1.3—a very commonly quoted piece of evidence.

Scaling Revisited

We first introduce scaling properties by analogy to the ordinary homogeneity requirements. In Chapter 1, these involved the *extensive* variables in the Gibbs function G as expressed by (see Section 1.3)

$$G(T, P; \lambda n_1, \lambda n_2, \dots, \lambda n_r) = \lambda G(T, P; n_1, n_2, \dots, n_r). \quad (7.2.1)$$

We now adopt this idea by applying it to the *intensive* variables close to criticality. We define

$$t \equiv T/T_c - 1, \quad p \equiv P/P_c - 1, \quad (7.2.2a)$$

and as a generalization of Eq. (7.2.1) introduce a scaling factor λ , replace t by $\lambda^{\zeta_t} t$, p by $\lambda^{\zeta_p} p$, and set

$$\mu(\lambda^{\zeta_t} t, \lambda^{\zeta_p} p) = \lambda \mu(t, p), \quad (7.2.2b)$$

showing how the scaling $t \rightarrow \lambda^{\zeta_t} t, p \rightarrow \lambda^{\zeta_p} p$ affects the chemical potential $\mu(t, p)$. This scaling process is still subject to the general chemical potential in the standard form

$$\mu(t, p) = -\tilde{S}T_c dt + \tilde{V}P_c dp, \quad (7.2.3a)$$

which we adapt to the scaling hypothesis by setting

$$\mu(\lambda^{\zeta_t} t, \lambda^{\zeta_p} p) = -\tilde{S}T_c \lambda^{\zeta_t} dt + \tilde{V}P_c \lambda^{\zeta_p} dp. \quad (7.2.3b)$$

where ζ_t and ζ_p are *scaling exponents* for the *scaling parameter* λ , all to be determined by experiment. Next, we first present a loose rationale for the present procedure. At the end of this section, we then put the analysis on a firmer footing.

Now carry out partial differentiations of the above with respect to p at constant t ,

$$\frac{\partial \mu(t, p)}{\partial p} = P_c \tilde{V}(t, p), \quad (7.2.4a)$$

and using Eq. (7.2.2b), we obtain

$$\frac{\partial \mu(\lambda^{\zeta_t} t, \lambda^{\zeta_p} p)}{\partial(\lambda^{\zeta_p} p)} \frac{\partial(\lambda^{\zeta_p} p)}{\partial p} = \lambda \frac{\partial \mu(t, p)}{\partial p} = \lambda P_c \tilde{V}(t, p) = \lambda^{\zeta_p} P_c \tilde{V}(\lambda^{\zeta_t} t, \lambda^{\zeta_p} p), \quad (7.2.4b)$$

which leads to the expression of interest

$$\lambda^{\zeta_p} \tilde{V}(\lambda^{\zeta_t} t, \lambda^{\zeta_p} p) = \lambda \tilde{V}(t, p). \quad (7.2.5)$$

No restriction has been imposed on the parameter λ . We take advantage of this freedom by selecting $\lambda = (-t)^{-1/\zeta_t}$ or $\lambda^{\zeta_t} t = (-t)^{-1}$, with $t < 0$, and then take the limit $P \rightarrow P_c$, that is, $p \rightarrow 0$. Such a choice is consistent with the requirement that correlations in fluctuations become very large near the critical point. Eq. (7.2.5) may then be solved for

$$\tilde{V}(t, 0) = (-t)^{(1-\zeta_p)/\zeta_t} \tilde{V}(-1, 0). \quad (7.2.6)$$

According to the abovementioned equation, close to the critical point, the molar volume of the fluid should change with temperature deviations as $-t$ raised to some power, which function is multiplied by a constant that is of no direct interest. This is our first step toward characterizing processes near criticality.

As a second step, let us return to Eq. (7.2.5) and set $t = 0$; then $\tilde{V}(0, p) = \lambda^{\zeta_p - 1} \tilde{V}(0, \lambda^{\zeta_p} p)$. Now select $\lambda = p^{-1/\zeta_p}$; thus

$$\tilde{V}(0, p) = p^{(1-\zeta_p)/\zeta_p} \tilde{V}(0, 1), \quad (7.2.7)$$

which indicates that near criticality the molar volume changes as p raised to some power, multiplied by a constant of no direct interest.

We now link the abovementioned results to experiment: Eqs. (7.2.6) and (7.2.7) hold separately for the liquid and vapor phases, hence the difference, $\tilde{V}_l - \tilde{V}_g \sim (-t)^{(1-\zeta_p)/\zeta_t}$, can be compared to the experimental data fitting of the form $\Delta \tilde{V} \sim (-t)^\beta$, which leads to the identification $\beta = (1-\zeta_p)/\zeta_t$. Eq. (7.2.7) may then be restated, relevant to the critical temperature, as $\Delta \rho \sim p^{(1-\zeta_p)/\zeta_p}$, where ρ represents the density. Comparison with the experimental data fitting process $\rho - \rho_c \sim \rho^{1/\delta}$ shows that $\delta = \zeta_p/(1-\zeta_p)$. The abovementioned relations for β and δ may be solved for

$$\zeta_t = -\frac{1}{\beta(\delta + 1)} \quad (7.2.8a)$$

and

$$\zeta_p = \frac{\delta}{1 + \delta}. \quad (7.2.8b)$$

These expressions specify the scaling exponents in terms of experimentally accessible parameters.

A second important result is based on the use of the relation¹ $\partial \mu / \partial \rho = (\tilde{V})^2 \chi_I / M_I$; κ_I is the thermal conductivity and $\chi_I \equiv 1/\kappa_I$. Now apply the same scaling hypothesis to the right-hand side of $\partial \mu / \partial \rho$ as was adopted in setting up Eq. (7.2.2). It follows that

$$\tilde{V}^2(\lambda^{\zeta_t} t, \lambda^{\zeta_p} p) \chi_I(\lambda^{\zeta_t} t, \lambda^{\zeta_p} p) = \lambda \tilde{V}^2(t, p) \chi_I(t, p). \quad (7.2.9)$$

When Eq. (7.2.5) is inserted, one obtains

$$\chi_I(\lambda^{\zeta_t} t, \lambda^{\zeta_p} p) = \lambda^{2\zeta_p-1} \chi_I(t, p). \quad (7.2.10)$$

Since there is no restriction on the choice for λ , we conveniently select the relation $\lambda = (-t)^{-1/\zeta_t}$ and set $p = 0$; then

$$\chi_I(t, 0) = (-t)^{(2\zeta_p-1)/\zeta_t} \chi_I(-1, 0). \quad (7.2.11)$$

This may be compared with the experimental data fit $\chi_I \sim |t|^{-\gamma}$, which shows how χ_I diverges near the critical point. We can thus identify

$$\gamma = (1 - 2\zeta_p)/\zeta_t. \quad (7.2.12)$$

In short, we have determined the scaling exponents in terms of several experimentally observed critical exponents; this provides a thermodynamic description of the properties of materials near their critical points.

The abovementioned procedures are not self-evident; at this stage, they may be justified by their success in quantifying experimental observations on materials near their respective critical points. At a more fundamental level, note that algebraic power laws are scale insensitive and therefore useful in dealing with critical phenomena. Consider $A t^b$ as a very elementary example. Squaring this function yields $A^2 t^{2b}$, which may be recast as $B \tau^b$, with the identifications $B = A^2$ and $\tau = t^2$. Thus the functional form is preserved but the initial factors have been rescaled.

This type of argument applies to certain classes of more general polynomial functions. For example, we will later encounter a *pair correlation function* that has the general form $G_c(r) = \langle O(0)O(r) \rangle_c$, where O is an *order parameter*, which depends on distance r , the function of which will be explained later. Suppose that we now rescale O by the scaling factor b^ω and introduce a new distance scale br , so as to generate a pair correlation function of the generalized form $G_c(br) = b^{2\omega} \langle O(0)O(br) \rangle_c$. Now insert the proper relation for the expectation value: $\langle O(0)O(br) \rangle_c = D/(b^{d-2+\eta})(r^{d-2+\eta})$, where D is a constant, d is the physical dimension of the system, and the exponent η is a quantity that arises in conjunction with critical phenomena. Thus $G_c(br) = b^{2\omega} D/(b^{d-2+\eta})(r^{d-2+\eta})$. Then by selecting $2\omega = d - 2 + \eta$, we reduce $G_c(br)$ to its original $G_c(r)$ form. This is simply a more sophisticated version of a rescaling process that leaves the original formulation unaltered. By way of contrast, such a scale invariance does not hold for exponential functions, for example.

A further heuristic argument proceeds as follows: in a régime where the correlation length ξ is very large compared to the atomic size, it should not matter whether the fundamental unit of length L is chosen to be 10 or 100 times the fundamental scale, so long as L remains appreciably smaller than ξ . This should be reflected in relating the Gibbs potential $G(t_s, p_s)$ for a relatively small volume L^3 to the same potential that pertains to the larger size $G(t_l, p_l)$, where t is the $(T - T_c)/T_c$ and where p is the $(P - P_c)/P_c$. It is reasonable to posit that $G(t_l, p_l) = L^d G(t_s, p_s)$, where d is the dimension of the system (three in this case). We next postulate that p should change linearly with size: as the cell area increases, so does the force required to maintain a steady pressure, but in a manner that accounts for the smaller effect of the surface area as the cell size is increased. This effect is addressed by assuming that $p_l = F_p(L)p_s$. A similar argument is adopted to write $t_l = F_t(L)t_s$; this ensures that t for the cell

goes critical when the system does. For the multiplying factor, we can reasonably assume that $F_p(L) \sim L^q$ and $F_t(L) \sim L^r$, with q and r unspecified. We are thus led to the relation $G(L^r t, L^q p) = L^d G(t, p)$, which is equivalent to Eq. (7.2.2).

Nevertheless, the abovementioned procedure may still seem artificial. However, there is a cross-check on the entire approach: insert Eq. (7.2.8) into (7.2.12) to obtain the following interrelation among scaling variables

$$\gamma = \beta(\delta - 1). \quad (7.2.13)$$

The abovementioned equation is known as *Widom's equality*. Its applicability has been tested and verified under many different conditions, thus vindicating the entire approach. In early work in this area, there was no reason to suspect the existence of any interrelation between critical exponents.

Several other relations may be cited; among them

$$\alpha + \beta(\delta + 1) = 2, \quad (7.2.14)$$

which will be derived in the next section, as will be

$$\alpha + 2\beta + \gamma = 2, \quad (7.2.15)$$

$$\gamma(\delta + 1) = (2 - \alpha)(\delta - 1). \quad (7.2.16)$$

Note once more that the critical exponents do not depend on the microscopic characteristics of any material. Therefore all data pertaining to their properties near the critical point should collapse onto a single curve, as is exemplified for fluids by Figure. 7.1.3. Other types of verification and tests are quoted in the literature, lending strong support to the basic soundness of the approach. In other words, we may assume the appropriateness of using relations such as Eqs. (7.2.6) – (7.2.16) in interpreting the properties of materials near their critical points. Of course, all this is shored up by mathematical derivations cited later.

Footnotes

7.2.1. See the derivation in footnote 7.1.5.

7.2.2. L. Kadanoff, *Physics* **2**, 263 (1966).

7.3 Derivation of Griffith's and Rushbrooke's Inequality

Here we derive Eq. (7.2.15) on the basis of somewhat tortuous thermodynamic arguments. An alternative, simpler procedure is provided in the next section, but the present method is instructive and included for that reason. Consider the liquid–gas phase diagram very close to the critical point, shown in Figure 7.3.1. One of the two isotherms is taken at the critical temperature T_c ; the other, at a lower temperature T_1 very close to T_c . We investigate the energy changes in going around two closed loops, MNSRM and LMRQL, so as to include the critical point in both traverses. To prevent excess proliferation of symbols we will, in the present section, assume that *all extensive quantities are molar variables*, thus omitting the tilde symbol here.

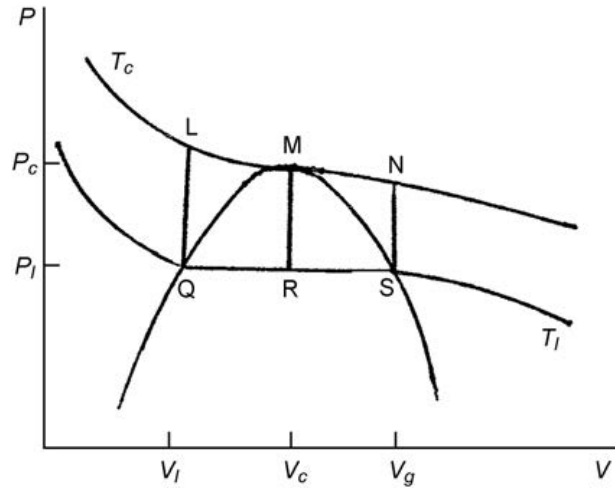


FIGURE 7.3.1

Pressure–volume diagram (schematic) for a fluid near its critical point. See text for details.

For the $M \rightarrow N$ segment, the energy change is given by

$$\Delta E_{NM} = T_c(S_N - S_M) - \int_{V_M}^{V_N} P(T_c) dV. \quad (7.3.1a)$$

Similarly, for $N \rightarrow S$ we find

$$\Delta E_{SN} = \int_{T_c}^{T_l} C_g dT, \quad (7.3.1b)$$

and for $S \rightarrow R$,

$$\Delta E_{RS} = T_l(S_R - S_S) - \int_{V_S}^{V_R} P(T_l) dV, \quad (7.3.1c)$$

while for $R \rightarrow M$,

$$\Delta E_{MR} = \int_{T_l}^{T_c} C_c dT. \quad (7.3.1d)$$

Next, write (l and g stands for liquid and vapor, respectively)

$$S_N - S_M \equiv (S_N - S_S) + (S_S - S_R) + (S_R - S_M), \quad (7.3.2a)$$

$$S_R = x_l S_Q + x_g S_S; \quad V_c = x_l V_l + x_g V_g; \quad x_l + x_g = 1, \quad (7.3.2b)$$

$$\frac{S_S - S_R}{V_g - V_c} = \left(\frac{dP}{dT} \right)_{T_1}. \quad (7.3.2c)$$

Then Eq. (7.3.1a) may be rewritten as

$$\Delta E_{NM} = T_c \left[\int_{T_1}^{T_c} \left(\frac{C_g}{T} \right) dT + (V_g - V_l) \left(\frac{dP}{dT} \right)_{T_1} + \int_{T_c}^{T_1} \frac{C_c}{T} dT \right] - \int_{V_M}^{V_N} P(T_c) dV, \quad (7.3.3a)$$

and Eq. (7.3.1c) becomes

$$\Delta E_{RS} = -T_1 (V_g - V_c) \left(\frac{dP}{dT} \right)_{T_1} - \int_{V_S}^{V_R} P(T_1) dV. \quad (7.3.3b)$$

Now sum around the closed loop MNSRM, for which the energy changes add to zero, and rearrange to find ($P(T_1)$ is a constant)

$$\begin{aligned} \int_{T_1}^{T_c} \frac{T_c - T}{T} C_c dT &= \int_{T_1}^{T_c} \frac{T_c - T}{T} C_g dT + (T_c - T_1)(V_g - V_c) \left(\frac{dP}{dT} \right)_{T_1} \\ &\quad - \int_{V_M}^{V_N} P(T_c) dV + P(T_1)(V_g - V_c). \end{aligned} \quad (7.3.4)$$

To the above, add and subtract $P_c(V_g - V_c)$ and rearrange to find

$$\begin{aligned} \int_{T_1}^{T_c} \frac{T_c - T}{T} C_c dT &= \int_{T_1}^{T_c} \frac{T_c - T}{T} C_g dT + \int_{V_M}^{V_N} (P_c - P) dV \\ &\quad + (T_c - T_1)(V_g - V_c) \left[\left(\frac{dP}{dT} \right)_{T_1} - \frac{P_c - P(T_1)}{T_c - T_1} \right]. \end{aligned} \quad (7.3.5)$$

Now carry out the same steps for the LMRQL loop, with the proviso that a minus sign enters at the LM and RQ stages relative to the MN and SR stages. We obtain

$$\begin{aligned} \int_{T_1}^{T_c} \frac{T_c - T}{T} C_c dT &= \int_{T_1}^{T_c} \frac{T_c - T}{T} C_l dT \\ &\quad + \int_{V_L}^{V_M} (P - P_c) dV - (T_c - T_1)(V_c - V_l) \left[\left(\frac{dP}{dT} \right)_{T_1} - \frac{P_c - P(T_1)}{T_c - T_1} \right]. \end{aligned} \quad (7.3.6)$$

Next, multiply Eq. (7.3.5) by $(V_g - V_c)^{-1}$ and Eq. (7.3.6) by $(V_c - V_l)^{-1}$; and then add the two. Then

$$\begin{aligned} \left(\frac{1}{V_g - V_c} + \frac{1}{V_c - V_l} \right) \int_{T_1}^{T_c} \frac{T_c - T}{T} C_c dT &= \frac{1}{V_g - V_c} \int_{T_1}^{T_c} \frac{T_c - T}{T} C_g dT + \frac{1}{V_c - V_l} \int_{T_1}^{T_c} \frac{T_c - T}{T} C_l dT \\ &+ \frac{1}{V_g - V_c} \int_{V_c}^{V_g} (P - P_c)_{T_c} dV + \frac{1}{V_c - V_l} \int_{V_l}^{V_c} (P - P_c)_{T_c} dV. \end{aligned} \quad (7.3.7)$$

Now, the first two terms on the right are positive definite. Therefore, on deleting them, the left-hand side becomes greater than the truncated right-hand side; which leads to the following inequality:

$$\left(\frac{1}{V_g - V_c} + \frac{1}{V_c - V_l} \right) \int_{T_1}^{T_c} \frac{T_c - T}{T} C_c dT > \frac{1}{V_g - V_c} \int_{V_c}^{V_g} (P_c - P)_{T_c} dV + \frac{1}{V_c - V_l} \int_{V_l}^{V_c} (P - P_c)_{T_c} dV. \quad (7.3.8)$$

Into the above equation, we now insert the following scaling relations:

$$|V - V_c| = B(T - T_c)^\beta \quad (B > 0), \quad (7.3.9a)$$

$$P - P_c = -D|V - V_c|^{\delta-1}(V - V_c) \quad (D > 0), \quad (7.3.9b)$$

$$C_c = A(T_c - T)^{-\alpha} \quad (A > 0). \quad (7.3.9c)$$

To satisfy the inequality (7.3.8), the two integrals on the right must be so formulated that the integrands remain positive. These two integrals then are required to have a form that may be evaluated by standard methods to yield

$$I_1 = (D/(V_g - V_c)) \int_{V_c}^{V_g} (V - V_c)^\delta dV = D(V_g - V_c)^\delta / (1 + \delta) \quad (7.3.10a)$$

and

$$I_2 = (D/(V_c - V_l)) \int_{V_l}^{V_c} (V_c - V)^\delta dV = D(V_c - V_l)^\delta / (1 + \delta). \quad (7.3.10b)$$

Then,

$$I_1 + I_2 = \frac{D}{1 + \delta} \left[(V_g - V_c)^\delta + (V_c - V_l)^\delta \right] = \frac{2DB^\delta T_c^{\beta\delta}}{1 + \delta} \left(1 - \frac{T}{T_c} \right)^{\beta\delta}. \quad (7.3.11)$$

In introducing the last step, we recognized that V_g and V_l are variables, whose place is taken by V in Eq. (7.3.9a).

In the integral on the left of Eq. (7.3.8), T_1 is supposed to be extremely close to T_c ; hence, no significant error is introduced in replacing T in the denominator of the integrand by T_c . We thus write

$$I_3 = A \int_{T_1}^{T_c} \frac{(T_c - T)^{1-\alpha}}{T_c} dT = AT_c^{1-\alpha} \int_{T_1/T_c}^1 \left(1 - \frac{T}{T_c} \right)^{1-\alpha} d\left(\frac{T}{T_c} \right) = \frac{AT_c^{1-\alpha}}{2 - \alpha} \left(1 - \frac{T_1}{T_c} \right)^{2-\alpha}. \quad (7.3.12)$$

Here T_1 is the variable quantity T very close to T_c . On introducing this relation on the left of Eq. (7.3.8) and using Eq. (7.3.11) on the right, we finally obtain

$$\left(1 - \frac{T}{T_c}\right)^{2-\alpha-\beta-\beta\delta} > \frac{DB^{1+\delta}(2-\alpha)}{A(1+\delta)} T_c^{\alpha+\beta(1+\delta)-1} \equiv L > 0. \quad (7.3.13a)$$

Last, we take logarithms on both sides to find

$$(2 - \alpha - \beta(1 + \delta)) \ln(1 - T/T_c) > \ln L. \quad (7.3.13b)$$

This must be examined carefully. T/T_c is very close to unity; hence, the logarithmic factor on the left becomes a hugely negative quantity. Thus, to preserve the inequality, two possibilities must be considered: (1) either $L > 1$, so that the right-hand side is positive and then for the inequality to remain effective, the multiplier of the logarithm on the left must be negative, so that necessarily $\alpha + \beta(1 + \delta) > 2$; (2) or $0 < L < 1$. In that event the right-hand side is negative. But we can make $\ln(1 - T/T_c)$ as negatively large as we please by moving T ever closer to T_c . There is then no way of satisfying the inequality except by demanding that the multiplier of the logarithmic term on the left vanish. Then $\alpha + \beta(1 + \delta) = 2$. We conclude that

$$\alpha + \beta + (1 + \delta) \geq 2, \quad (7.3.14)$$

which is *Griffith's inequality*.

On inserting numerical values into Eq. (7.3.14), one obtains $\alpha + \beta(1 + \delta) = 2.000 \pm 0.022$, equal to the value 2 within experimental error. In fact, by adopting the static scaling hypothesis in common use in statistical mechanics, one finds that the inequality (7.3.15) is replaced by an equality, as specified by Eq. (7.2.14). We also prove this assertion below by a different approach, which exemplifies once more that critical phenomena do not depend on the physical characteristics of the system.

Rushbrooke's inequality, based on magnetization phenomena, is far easier to obtain. By comparing the analogous relations $dE = TdS - PdV$ and $dE = TdS + \mathcal{H}_0 d\mathbf{M}$, one readily converts Eq. (1.15.7) into the form

$$C_{\mathcal{H}} - C_{\mathbf{M}} = T(\partial\mathbf{M}/\partial T)_H^2 / (\partial\mathbf{M}/\partial\mathcal{H}_0)_T. \quad (7.3.15)$$

On the left, we omit the positive term $C_{\mathbf{M}}$, so that the equality is replaced by an *inequality*. We also introduce the conventional relations

$$\mathbf{M} = B(1 - T/T_c)^\beta, \quad (B > 0, T < T_c), \quad (7.3.16a)$$

$$(\partial\mathbf{M}/\partial\mathcal{H}_0)_T = \chi_0 = D(1 - T/T_c)^{-\gamma}, \quad (D > 0, T < T_c), \quad (7.3.16b)$$

$$C_{\mathcal{H}} = A(1 - T/T_c)^{-\alpha}, \quad (A > 0), \quad (7.3.16c)$$

which reflect how the magnetization approaches zero and the magnetic susceptibility and heat capacity diverge as the critical temperature is approached from below. On inserting Eqs. (7.3.16) into the inequality (7.3.15), we obtain

$$(1 - T/T_c)^{-\alpha-2(\beta-1)-\gamma} > T\beta^2 B^2 / T_c^2 A D \equiv Q, \quad (7.3.17a)$$

and on taking logarithms we find

$$-(\alpha + 2(\beta - 1) + \gamma) \ln(1 - T/T_c) > \ln Q. \quad (7.3.17b)$$

This inequality is handled precisely in the same manner as Eq. (7.3.13b). If $Q > 1$ then the left-hand quantity in square brackets has to remain positive; if $0 < Q < 1$ then this quantity must vanish. We therefore find that

$$\alpha + 2\beta + \gamma \geq 2, \quad (7.3.18)$$

which is known as *Rushbrooke's inequality*. Again, one finds that given the numerical values for the critical exponents, this relation holds as an equality. This will also be verified below by considering magnetic properties of materials near their critical points. In addition, you should be able to show, starting with Eq. (1.14.7), that Eq. (7.3.18) also holds for fluids.¹

Equation (7.2.16b) is now obtained by combining Eqs. (7.2.14 and 7.2.15).

Magnetic Properties Near the Critical Point

To drive home the point that critical phenomena for different physical situations are analyzed in the same manner, and to convert the above inequalities into equalities, we now consider the magnetic characteristics of material close to the temperature at which magnetic order gives way to disorder. We begin with the truncated Gibbs free energy $dG = -SdT - M d\mathcal{H}$; to avoid encumbering the notation, *we here omit the subscript 0 from \mathcal{H}* . We have also quietly dropped the pressure term P_m that includes the magnetic contribution, as specified by Eq. (5.8.4). For small magnetic fields, this condition may be approximated by keeping the mechanical pressure fixed. Note the parallelism with the case of fluids. Much of what follows is a recapitulation of the derivations appropriate for fluids. The starting point is the scaling relation $H \equiv (\mathcal{H} - \mathcal{H}_c)/\mathcal{H}_c$ so as to write

$$G(\lambda^{a_t} t, \lambda^{a_H} H) = \lambda G(t, H), \quad (7.3.19)$$

where $t \equiv (T - T_c)/T_c$. Now differentiate with respect to H :

$$\lambda^{a_H} \frac{\partial G(\lambda^{a_t} t, \lambda^{a_H} H)}{\partial (\lambda^{a_H} H)} = \lambda \left(\frac{\partial G(t, H)}{\partial H} \right). \quad (7.3.20)$$

On executing the partial differentiations, one finds that $M = (M - M_c)/M_c$, which leads to the scaled equation

$$\lambda^{a_H} M(\lambda^{a_t} t, \lambda^{a_H} H) = \lambda M(t, H). \quad (7.3.21)$$

We now set $H = 0$ and note that the above relation must hold for any λ of our choice, and in particular, for $\lambda = (-1/t)^{1/a_t}$. Then

$$M(t, 0) = (-t)^{(1-a_H)/a_t} M(-1, 0). \quad (7.3.22)$$

This may be compared to experimental observation: as $t \rightarrow 0^-$ it is found empirically that $M \sim (-t)^\beta$, whence

$$\beta = (1 - a_H)/a_t. \quad (7.3.23)$$

Next, set $t = 0$ in Eq. (7.3.21) and adopt the choice $\lambda = H^{-1/a_H}$, whereby

$$M(0, H) = \lambda^{(1-a_H)/a_H} M(0, 1). \quad (7.3.24)$$

For small fields, one finds empirically that $|\mathcal{H}| \sim M^\delta$, whence we obtain

$$\delta = a_H / (1 - a_H). \quad (7.3.25)$$

These two last relations may be solved for

$$a_t = 1/\beta(1 + \delta) \quad \text{and} \quad a_H = \delta/(1 + \delta), \quad (7.3.26)$$

thereby linking the critical exponents to experimental parameters.

We now carry out a second differentiation of the Gibbs potential, Eq. (7.3.20), with respect to H to obtain the magnetic susceptibility χ (we again omit the subscript 0). This leads to the result

$$\lambda^{2a_H} \chi(\lambda^{a_t} t, \lambda^{a_H} H) = \lambda \chi(t, H). \quad (7.3.27)$$

Then set $H = 0$ and take $\lambda = (-t)^{-1/a_t}$; this leads to

$$\chi(t, 0) = (-t)^{-(2a_H-1)/a_t} \chi(-1, 0). \quad (7.3.28)$$

This formulation may be compared to the empirical relation $\chi \sim (-t)^{-\gamma', -\gamma}$ for $T < T_c$ and $T > T_c$ respectively. We then see that

$$\gamma' = (2a_H - 1)/a_t, \quad (7.3.29)$$

so that when we insert Eq. (7.3.26) we obtain

$$\gamma' = \beta(\delta - 1), \quad (7.3.30)$$

which is Widom's equality. The same argument may be made to obtain γ .

We return to the relation specifying $G(T, H)$ and differentiate twice with respect to T to obtain $-C_H/T$. Translating to the scaled variable equation, we find that

$$\lambda^{2a_t} C_H(\lambda^{a_t} t, \lambda^{a_H} H) = \lambda C_H(t, H). \quad (7.3.31)$$

$$\text{Now set } H = 0, \lambda = (-t)^{-1/a_t}, \quad (7.3.32)$$

which converts the above to the form

$$C_H(t, 0) = (-t)^{(1-2a_t)/a_t} C_H(-1, 0). \quad (7.3.33)$$

Experimentally it is found that the variation of heat capacity with deviation from the critical temperature proceeds as $C_H \sim (-t)^{-\alpha'}$. This immediately establishes the correspondence

$$\alpha' = (1 - 2a_t)/a_t. \quad (7.3.34a)$$

When substituting from Eq. (7.3.26) one obtains

$$\alpha' + \beta(1 + \delta) = 2, \quad (7.3.34b)$$

which is Rushbrooke's relation as an equality.

Many other interrelations between various types of critical exponents have been derived, but we refer the reader to other sources¹ for an exhaustive listing.

Reference and Exercise

7.3.1. See References in Footnote 7.1.1.

7.3.2. Show that Eq. (7.3.18) is recovered when considering fluids as a working substance. What do you conclude from your analysis?

7.4 Scaled Equation of State

It is possible to establish a scaled equation of state for magnetic materials near their critical points along the following lines: We return to Eq. (7.3.21) and set $\lambda = (-t)^{-1/a_t}$, such that

$$M(t, H) = |t|^{(1-a_H)/a_t} M\left(\frac{t}{|t|}, \frac{H}{|t|^{a_H/a_t}}\right). \quad (7.4.1)$$

Now introduce Eq. (7.3.23) and rewrite the above in the form

$$\frac{M(t, H)}{|t|^\beta} = M\left(\frac{t}{|t|}, \frac{H}{|t|^{\beta\delta}}\right). \quad (7.4.2)$$

This represents a very interesting finding: let us introduce a scaled magnetization of the form $m \equiv |t|^{-\beta} M(t, H)$, and a scaled magnetic field of the form $h \equiv |t|^{-\beta\delta} H$; then the above relationship becomes

$$m = m(\pm 1, h), \quad (7.4.3)$$

or in inverse form,

$$h = h(\pm 1, m). \quad (7.4.4)$$

According to this analysis, the scaled relations involve solely one independent variable. Then sets of magnetization data plotted in the above manner should lie on two branches of a single curve, depending on whether $T > T_c$ or $T < T_c$. This rationalizes the collapse of magnetic data sets encountered experimentally, as long as one is “sufficiently close” to the critical temperature. Analogous relations apply to the study of fluids close to their critical point. In fact, this type of data collapse is taken to be a warrant for the applicability of the current theories of critical phenomena. An example of this effect is provided by the electrical conductivity in Cr-doped V_2O_3 , which is fine tuned by the application of pressure to be very close to the critical transition between the metallic and insulating state.¹

Reference

7.4.1. P. Limelette, A. Georges, D. Jerome, P. Wzietek, X. Yao, J.M. Honig, Science, **302**, 89 (2003).

7.5 Landau Theory of Critical Phenomena and Phase Transitions

Generalities

In this section, we study an approach to critical phenomena and phase transitions pioneered by Landau, which encompasses aspects of order–disorder theory and the discussions of Sections 7.1 and 7.2. The study is not based on any specific models and therefore qualifies as a thermodynamic theory. The fundamental quantity of interest is the *order parameter*, η , as the characteristic variable to describe the degree of ordering in a material transitioning from a completely ordered arrangement of the constitutive elements, $\eta=1$, at extremely low temperatures, to an absolutely disordered configuration, $\eta=0$, at highly elevated temperatures. The most elementary example is the idealized ferromagnet, the spins of which are completely aligned at liquid helium temperatures, and which becomes completely demagnetized beyond the Curie temperature. In many materials the increase in disorder is accompanied by either gradual or abrupt changes in phase, as explained in conjunction with phase diagrams, as well as by alterations in symmetry. It is such changes that the Landau theory describes in the mean-field approximation.

We begin with Landau by assuming that for small departures from the relevant critical or transition point, the thermodynamic properties of the system may be described in terms of a functional \mathcal{L} that features an ascending power series in η , where $\eta=0$ at the critical transition point. We thus write

$$\mathcal{L} = a_0 + a_1\eta + a_2\eta^2 + a_3\eta^3 + a_4\eta^4 + \dots \quad (7.5.1)$$

where \mathcal{L} becomes the Gibbs free energy of the system after η has been optimized. The constant, a_0 , being the value of \mathcal{L} for $\eta = 0$, is of little current interest; henceforth we treat $\mathcal{L} \rightarrow \mathcal{L} - a_0$ as the excess functional beyond the background value. Eq. (7.5.1) has enormous flexibility. Depending on the choice for the parameters a_1, \dots, a_4 , one obtains a considerable variety of curves displayed in Figure 7.5.1 that you should carefully examine. These curves mimic the ones displayed in Sections 3.8–3.10. Note that the various shapes are achieved with the choice $a_3=0$.

The utility of Eq. (7.5.1) is perhaps the best gauged by examining the generic pressure–volume phase diagram of Figure 7.5.2. Entered as inserts in the various regions are the forms assumed by the molar Gibbs free energy $\tilde{G}(V)$ when the volume of the phase is caused to deviate from its equilibrium value at the minimum of each diagram. Away from the T – C phase boundary and for $T < T_c$, these Gibbs potentials exhibit two asymmetric minima (1, 2, 3) associated with the liquid and vapor phases. At the boundary separating the phases (4), these minima are symmetric, reflecting the equality of the chemical potentials in the two-phase configuration. At the critical point T_c (5), one encounters a shallow, essentially flat bottom, and away from that condition (6), one may find a skewed configuration. The Gibbs potential for the one-phase fluid (7) is U shaped. Thus Landau’s approach should be useful in dealing with the various phenomenological aspects of phase transitions. To make contact with physical properties, it is assumed that at least some of the coefficients in Eq. (7.5.1) depend parametrically on temperature, and, if needed, on other variables such as pressure or magnetic fields.

We now examine several operating conditions that correspond to the various curves displayed in Figure 7.5.2. We do this by optimizing \mathcal{L} via the equilibrium constraint

$$\partial\mathcal{L}/\partial\eta = 0 = a_1 + 2a_2\eta + 3a_3\eta^2 + 4a_4\eta^3 + \dots \quad (7.5.2)$$

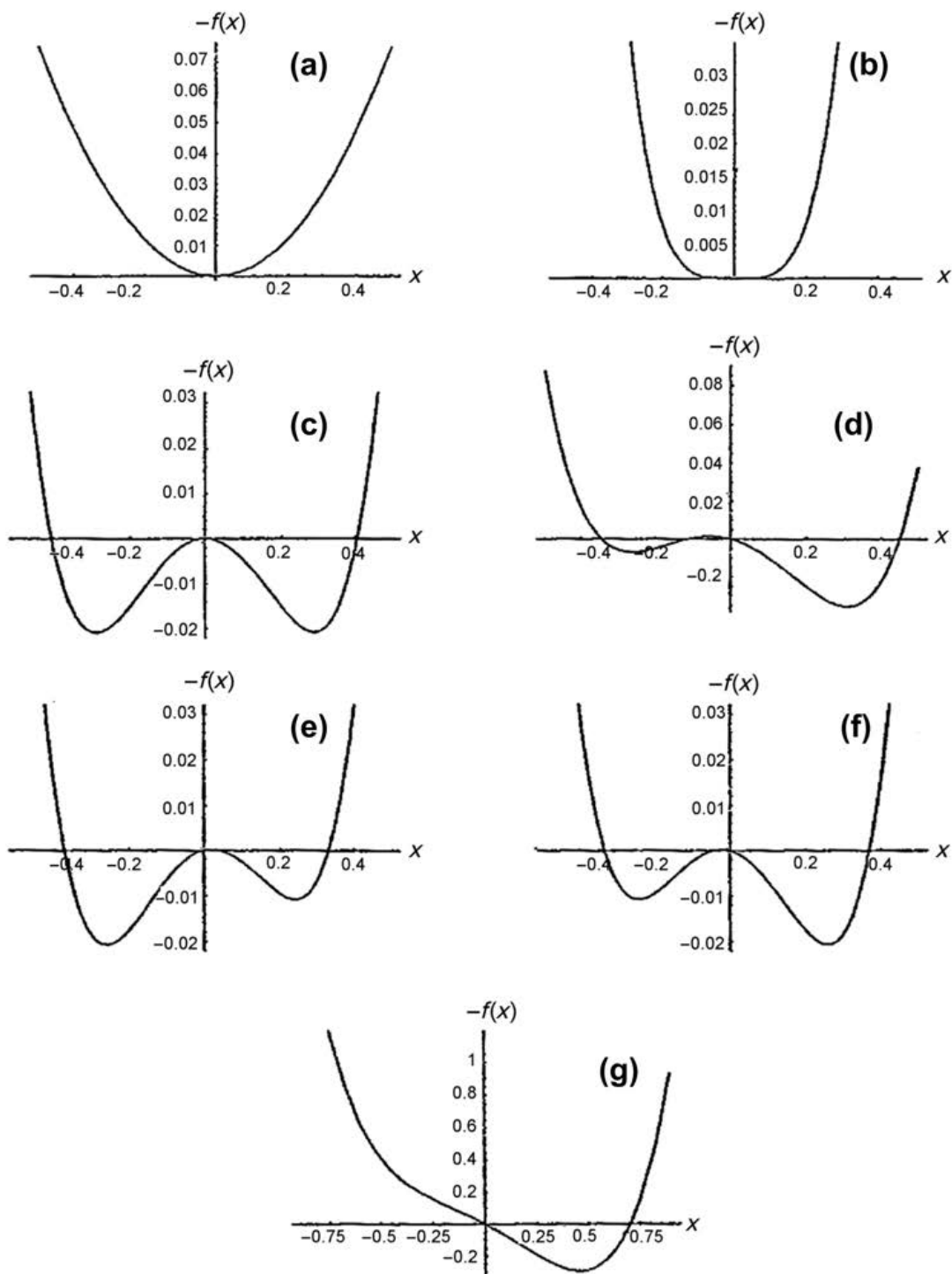


FIGURE 7.5.1

Plots of $f(x) = ax + bx^2 + cx^3 + dx^4$ for a variety of coefficients: (a) $a=0, b=-0.3, c=d=0$; (b) $a=b=c=0, d=-5$; (c) $a=0, b=0.5, c=0, d=-3$; (d) $a=0.05, b=0.5, c=0, d=-3$; (e) $a=-0.02, b=0.5, c=0, d=-4$; (f) $a=0.02, b=0.5, c=0, d=-4$; (g) $a=0.7, b=0.5, c=0, d=-3$. Similar curves are obtained on setting $a=0$, and allowing c to vary.

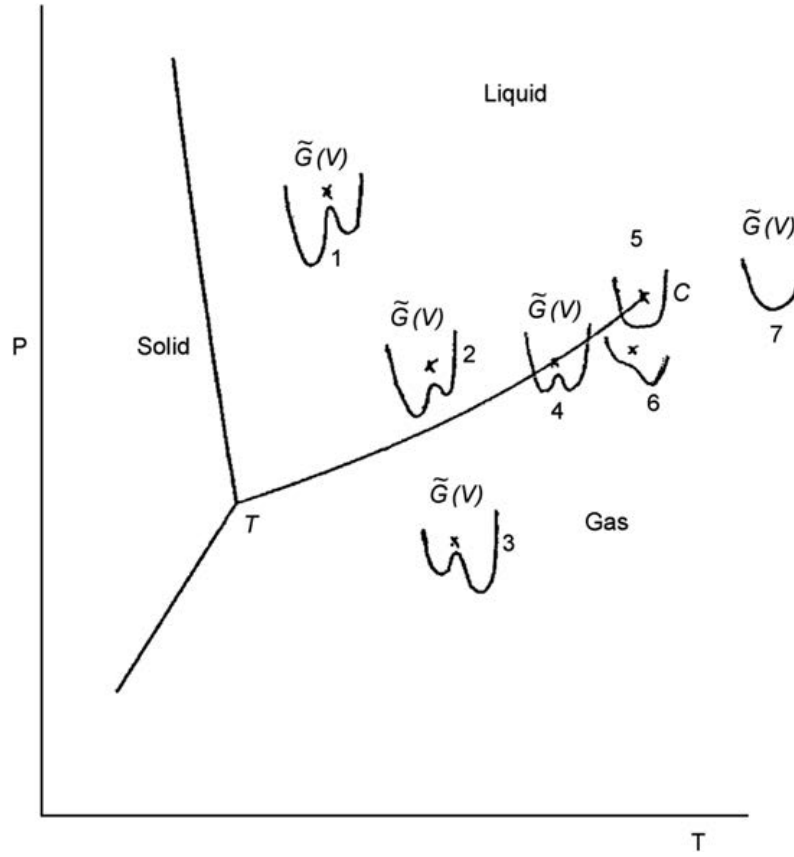


FIGURE 7.5.2

Generic phase diagram for a one-component system, showing at various locations how the Gibbs free energies change when the volume is displaced from its equilibrium value. The latter curves are well reproduced by the Landau functions displayed in Figure 7.5.1.

At equilibrium the Gibbs free energy is a minimum; for the derivative to vanish with $\eta=0$, we must set $a_1=0$.

Expansion in Even Powers of the Order Parameter

We first consider the isotropic case where \mathcal{L} is an even function of η , which implies the absence of external constraints that impart a direction to the approach to the critical point. On thus setting $a_3=0$ in Eqs. (7.5.1) and (7.5.2), we obtain

$$a_2 + 2a_4\eta^2 = 0. \quad (7.5.3)$$

The coefficients a_2 and a_4 are considered as parameters that generally vary with the deviation of the system from the criticality. Thus if temperature is the relevant control variable, we may expand the parameter, with the leading term reading

$$a_2 \equiv a_2(T) = a_2^0 + \left[\frac{(T - T_c)}{T_c} \right] a_2' + \dots \quad (7.5.4a)$$

where the prime indicates a partial derivative of a_2 with respect to T , evaluated at $T=T_c$. Similarly,

$$a_4(T) = a_4^0 + \left[\frac{(T - T_c)}{T_c} \right] a_4' + \dots \quad (7.5.4b)$$

The expansion term in a_4' is usually neglected because it represents second-order effects that are ignored; thus we regard a_4 as a parameter.

Also, in conformity to earlier discussion, we require that $\eta=0$ for $T \geq T_c$, and $\eta > 0$ for $T < T_c$. The solution of Eq. (7.5.3) then reads

$$\eta_0 = 0, \quad (T \geq T_c) \quad \text{or} \quad \eta_0 = \sqrt{(-a_2(T)/2a_4)}, \quad (T < T_c). \quad (7.5.5)$$

But while η_0 is to be nonzero in the range $T < T_c$, we must set $a_2^0=0$ so that with increasing temperature η_0 vanishes at $T=T_c$. Then η_0 varies as $\sqrt{((T_c - T)/T_c)}$ for $T < T_c$. This coincides with the change in volume with temperature of a fluid, Eq. (7.1.6). For that particular case, it invites the identification of η_0 with $(V - V_c)/V_c$. We have thus endowed the order parameter with a physical interpretation.

This approach also pertains to the phase transformation in a solid that is the result of a gradual displacement of atoms from their original position in a “soft mode” transition. For simplicity, we adopt a one-dimensional model and suppose that the gradual shift with temperature in atomic location may be correlated with anharmonic terms in the lattice vibration of the participating atoms. This is quantified via the relation $V = V_2 x^2 - V_4 x^4$ for the potential energy in terms of the displacement x of each oscillator from its equilibrium position. This represents a first-order expansion for the anharmonic term. In the present approximation, we replace the x^4 term by $\langle x^2 \rangle x^2$, where the quantity in angular brackets is an averaged displacement variable, given by $k_B T / V_2$, where k_B is Boltzmann’s constant. Thus we find that $V = V_2 x^2 - V_4 x^4 = [V_2 - k_B T V_4 / V_2] x^2$, from which one deduces that the vibration frequency varies as $\nu \sim [V_2 - k_B T V_4 / V_2]^{1/2}$, which is of the form $\nu \sim \nu_0 (1 - AT)^{1/2}$ that is in consonance with the formulation (7.5.5). Surprisingly, soft mode transitions do indeed conform to this very simple model. The transformation is complete at $T=T_c$, where $\nu=0$. Here the identification of η_0 with ν is appropriate.

Relation to Thermodynamics

The general connection with thermodynamics is established by allowing the a_2 parameter to vary with temperature as $a_2(T) = (1/2)a(T - T_c) \equiv (1/2)at_c$, which provides a first-order linear temperature departure of the system from criticality. We redefine the parameter as $a_4 = (1/4)b$. The Landau functional then reads

$$\mathcal{L} = \frac{1}{2}at_c\eta^2 + \frac{1}{4}b\eta^4. \quad (7.5.6)$$

Representative plots of \mathcal{L} versus η are shown in Figure 7.5.3. One should note the changeover in the curves from a display of a single minimum at $\eta = 0$ for $T \geq T_c$ to a double minimum in the range $T < T_c$. This is occasioned by the sign change in t_c at the critical temperature.

The intersections of the graphs with the vertical line at the specific value η_a trace the variation of $\mathcal{L}(\eta_a)$ with temperature as one proceeds from lower to higher temperatures.

We now introduce the conventional enthalpy and entropy terms via $\mathcal{L} = \Delta H_c - T\Delta S_c$, which gives rise to

$$\Delta H_c = -\frac{1}{2}at_c\eta^2 + \frac{1}{4}b\eta^4; \quad \Delta S_c = -\frac{1}{2}a\eta^2. \quad (7.5.7)$$

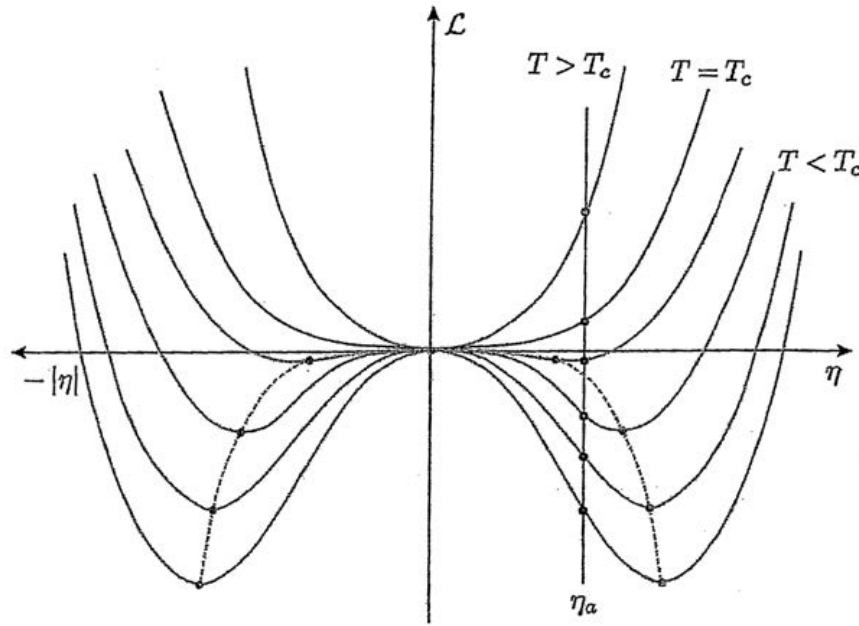


FIGURE 7.5.3

Schematic representations of Eq. (7.5.6), showing how the single minimum in the function for $T \geq T_c$ changes to a double minimum for $T < T_c$. The vertical line shows how the Landau free energy changes with the order parameter η_a before optimization; the minima show the Gibbs free energy density as a function of η_0 after optimization.

Equilibrium Constraints

The next step involves imposition of the equilibrium constraint $\partial \mathcal{L} / \partial \eta = 0$, which yields

$$a(T - T_c)\eta_0 + b\eta_0^3 = 0, \quad (7.5.8)$$

as the equilibrium value for η_0

$$\eta_0 = 0 \quad (T \geq T_c) \quad \text{or} \quad \eta_0 = \pm \sqrt{\frac{a(T_c - T)}{b}} \equiv \pm \left(\frac{-at_c}{b} \right)^{1/2}, \quad (T \leq T_c). \quad (7.5.9)$$

We discard negative and complex solutions as unphysical. To keep η_0 real, we need $a/b \geq 0$; in setting up Eq. (7.5.1), we implicitly assumed that $a > 0$, thus rendering $b > 0$. The $\eta_0 \sim \sqrt{T_c - T}$ dependence is characteristic of mean-field theory. Eq. (7.5.9) specifies the value of the order parameter under equilibrium conditions. When applied to Eq. (7.5.6), we convert the Landau free energy to the excess Helmholtz thermodynamic free energy density. However, in dealing with condensed phases, one may ignore the small difference between Helmholtz and Gibbs free energies. This allows us to use temperature and pressure as the two relevant control variables. The Gibbs excess free energy density thus reads

$$\Delta G_c = 0, t_c \geq 0; \quad \Delta G_c = \frac{1}{4} \frac{a^2 t_c^2}{b}, \quad t_c < 0, \quad (7.5.10)$$

showing that below T_c , the free energy is a parabolic function of temperature.

The entropy density in excess of the background value is found from Eq. (7.5.7) as

$$\Delta S_c = -a^2(T_c - T)/2b. \quad (7.5.11)$$

which shows that close to the critical point the configurational entropy varies with temperature as $(a^2/2b)T$, and that we require $b > 0$, so as to keep S_c positive. Furthermore, ΔS_c changes smoothly to zero at T_c , whereas the first derivative of ΔS_c exhibits a discontinuity, indicative of a higher order transition.

The excess heat capacity density at constant pressure close to the critical point can be worked out from the usual relation $C_p = T(\partial\Delta S_c/\partial T)$ to yield

$$C_p = \left(\frac{a^2}{2b}\right)T, \quad T \rightarrow T_c^-. \quad (7.5.12)$$

Above T_c the excess heat capacity vanishes; thus at T_c , C_p is discontinuous. This immediately points to a difference with experiment: the heat capacity at the critical point actually exhibits a singularity.

A brief review of the salient features of Figure 7.5.3 may be of assistance: as already stated, the vertical line η_a intersecting with the curves shows how the $\mathcal{L}(\eta_a)$ functional changes with temperature. However, the equilibrium constraints completely alter the situation since the order parameter now changes with temperature as well. The free energy is then represented as a progression of specific $\eta_0(T)$ along the minima until these converge on zero at $T = T_c$. Those familiar with phase diagrams immediately recognize that the region in Figure 7.5.3 under the dome is inaccessible to the system. For, the Landau functional should always increase with $|\eta|$ because the entropy diminishes and the enthalpy rises with increasing order. This runs counter the situation under the dome; thus the corresponding η values are not encountered at equilibrium. This is a neat illustration of how the Landau theory relates to phase diagrams of Chapter 3 in the vicinity of a critical point.

Effects Encountered in External Constraints

In an extension of the abovementioned treatment, we now introduce anisotropy effects; for clarity, we deal with the particular case of a material subjected to an external magnetic field \mathcal{B} , but the analysis is easily generalized. The linear response in this case is the magnetization density $\langle S^z \rangle \equiv \mathcal{M} \equiv \eta$, which functions as the relevant order parameter. When the magnetization is aligned with the field, the energy of the system changes by $-\mu\mathcal{M}\mathcal{B}$. Accordingly, the Landau functional (7.5.6) now reads

$$\mathcal{L} = -\mu\mathcal{B}\eta + \frac{1}{2}at_c\eta^2 + \frac{1}{4}b\eta^4. \quad (7.5.13)$$

This small change introduces enormous flexibility that is perhaps the best explored by use of diagrams. We follow the exposition by Goldenfeld.³ Figure 7.5.4 shows a set of \mathcal{L} versus η diagrams arranged in three columns labeled $\mathcal{B} < 0, \mathcal{B} = 0, \mathcal{B} > 0$. The three rows top to bottom depict the $\mathcal{L}(\eta)$ dependence for the cases $T > T_c, T = T_c, T < T_c$. The heavy dots locate the equilibrium configuration.

As before, for $T \geq T_c$ and for $\mathcal{B} = 0$, the equilibrium free energy in excess of the ground value occurs at the single minimum of the order parameter at $\eta_0 = 0$. As we move left to right across either the first or second row, the change from negative to positive \mathcal{B} is accompanied by a shift from negative to positive η_0 values. The concomitant changes in Landau potentials should be noted, reflecting the

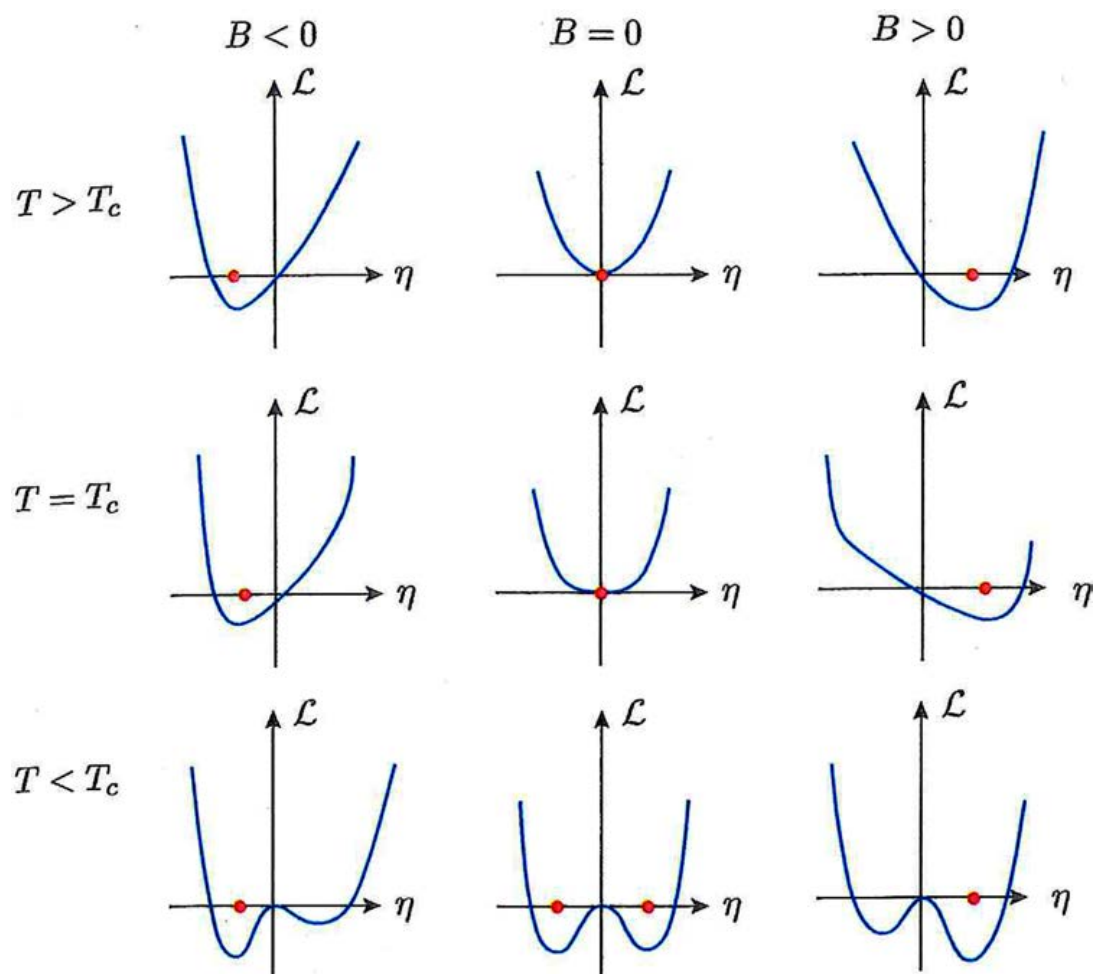


FIGURE 7.5.4

Sketches of the Landau free energy density at temperatures above, at, and below the critical temperature in the absence of a magnetic field, and for different orientations of an applied magnetic field. The heavy dots indicate the value of the order parameter for which the thermodynamic free energy is minimized. Reproduced from N. Goldenfield, *Lectures on Phase Transitions and the Renormalization Group*, Copyright Westview Press of Perseus Books Group; reprinted with permission.

effects of the applied magnetic field. The bottom row displays the magnetic-field effects in the $T < T_c$ regime. As discussed earlier, the symmetrically arranged double minimum at $B = 0$ involves a thermodynamically inaccessible region between the minima. When the magnetic field is applied, this symmetry is broken, and only a single minimum is encountered, the position of which reflects the direction of the field. On the other hand, going down the central column shows the change in \mathcal{L} with decreasing T in zero field, which pictorially summarizes the discussion of Figure 7.5.3 in the preceding section.

Analytical Representations

We now consider the analytical representation that includes magnetic-field effects. On imposing the requirement $\partial\mathcal{L}/\partial\eta = 0$ onto Eq. (7.5.13), we find that

$$at_c\eta_0 + b\eta_0^3 = at_c\mathcal{M} + b\mathcal{M}^3 = \mu\mathcal{B}. \quad (7.5.14)$$

At the critical point $t_c = 0$; then the above reduces to

$$\mathcal{M} = \left(\frac{\mu}{b}\right)^{1/3} \mathcal{B}^{1/3}, \quad (7.5.15)$$

so that at the critical point in conventional notation, $\mathcal{M} \sim \mathcal{B}^\delta$, $\delta = 1/3$.

We study magnetization effects via the isothermal magnetic susceptibility $\chi_T = \partial\mathcal{M}/\partial\mathcal{B}$, where $\mathcal{M} = N\mu^2\mathcal{M}$ is the total magnetization of the system of N constituents. We first differentiate Eq. (7.5.14) with respect to \mathcal{B} to find

$$(at_c + 3b\eta_0^2) \frac{\partial\mathcal{M}}{\partial\mathcal{B}} = \mu, \quad (7.5.16)$$

where in very weak magnetic fields the isothermal magnetic susceptibility is found to be

$$\chi_T = \left(\frac{\partial N\mu^2\mathcal{M}}{\partial\mathcal{B}}\right) = \frac{N\mu^2}{at_c + 3b\eta_0^2}, \quad (7.5.17)$$

where η_0 is the solution to Eq. (7.5.14). We encounter two possibilities

$$\text{For } t_c \geq 0, \quad \eta_0 = 0 \quad \text{and} \quad \chi_T = \frac{N\mu^2}{at_c}; \quad (7.5.18a)$$

$$\text{For } t_c < 0, \quad \eta_0^2 = -\frac{at_c}{b} \quad \text{and} \quad \chi_T = -\frac{N\mu^2}{2at_c}, \quad (7.5.18b)$$

where we introduced an approximation via the use of Eq. (7.5.9). The abovementioned relations represent the Curie–Weiss law. The abovementioned versions differ numerically by a factor of 2. A comparison with the mean-field index indicates that $\gamma = 1$, an elegant method that supplants the more cumbersome earlier derivations based on specific models.

Hysteresis Effects via the Landau Theory

The abovementioned presentation allows for a qualitative discussion of hysteresis effects, based on sketches of Eq. (7.5.14) for \mathcal{B} as a function of $\eta \equiv \mathcal{M}$. As shown in Figure 7.5.5(a), above T_c the plot involves a simple sigmoidal shape; below T_c the insulator shape of Figure 7.5.5(b) provides for the possibility of having the same magnetic field \mathcal{B}_u or \mathcal{B}_l coincide with the maximum or minimum of the curve. Where these \mathcal{B} values intersect with the curve, the intermediate magnetizations are unstable, indicative of hysteresis effects that are visualized by rotating the diagram counterclockwise by 90° and then by 180° about the η axis.

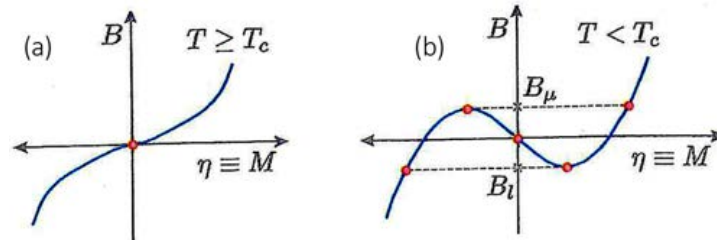


FIGURE 7.5.5

Diagrams illustrating the origin of magnetic hysteresis based on Landau theory; for explanations see the text.

Pressure–Volume Variations Near the Critical Point

Just as the magnetization density is the order parameter corresponding to the magnetic field, so may the (excess relative) volume V of a liquid be taken as the order parameter corresponding to the (excess relative) pressure P . This invites the analogy $\mathcal{B} \rightarrow P$ and $\eta = \mathcal{M} \rightarrow \eta = V$. On applying this analogy to the abovementioned discussion, one obtains the following results

$P = 2bV^3$, which is equivalent to Eq. (7.1.7),

$V = \sqrt{(2a/b)} (-t)^{1/2}$, which is equivalent to Eq. (7.1.6)

$$\left(\frac{\partial V}{\partial P} \right)_T = \kappa_I V = 1/2at, \quad 1/4a \cdot (-t). \quad (7.5.19)$$

In the same spirit, one may also consider the (relative excess) entropy S to be the order parameter corresponding to the (relative excess) temperature t . This leads to the following result for the (relative excess) heat capacity

$$\frac{\Delta C_P}{T} = 1/2at, \quad 1/4a \cdot (-t), \quad (7.5.20)$$

which is in reasonable agreement with Eq. (7.1.10). Thus all results specified by standard techniques in the mean-field approximation for experimental observation of critical phenomena have been reproduced earlier with far less effort.

Adaptation to the First-Order Phase Transitions

We now enlarge on the flexibility of the previous discussion by including a cubic term in the representation of the Landau free energy. We set

$$\mathcal{L} = \frac{1}{2}at_c\eta^2 + \frac{1}{4}b\eta^4 - \frac{1}{3}c\eta^3, \quad \left(a > 0, b > 0, c > 0 \right). \quad (7.5.21)$$

(I) (II) (III)

The Roman numerals serve for identification purposes.

A series of representative sketches of \mathcal{L} versus η are shown in Figure 7.5.6, for a set of decreasing temperatures going top to bottom. It is seen that at high temperatures, one encounters a nearly

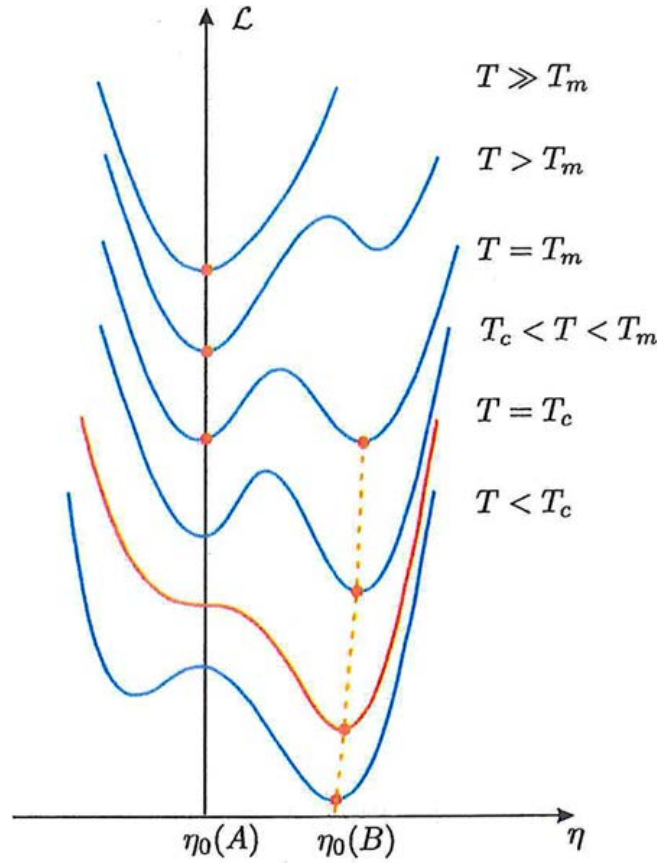


FIGURE 7.5.6

Representative sketch of Eq. (7.5.21); note the appearance of a double minimum at $T = T_m$, indicative of a phase transition.

parabolic curve with a specific minimum value, \mathcal{L}_s , characteristic of state A. On lowering the temperature the negative contribution via term (III) becomes noticeable, resulting in a secondary minimum, \mathcal{L}_1 , which drops further until it coincides with \mathcal{L}_s , at T_m , where the two minima match. As discussed next, the order parameter jumps discontinuously from $\eta = 0$ to a positive value, indicative of a first-order transition; the intermediate range of η is inaccessible. With further decreases in temperatures in the range $T < T_m$, we deal with the system in state B. At temperature T_c term (I) changes sign, and at lower temperatures the upper minimum becomes irrelevant.

For a quantitative analysis, we impose the equilibrium requirement

$$b\eta_0^3 - c\eta_0^2 + a(T - T_c)\eta_0 = 0, \quad (7.5.22)$$

a cubic equation with the solutions

$$\eta^0 = 0 \quad \text{and} \quad \eta_0(T) = \frac{c}{2b} \pm \sqrt{\left(\frac{c}{2b}\right)^2 - \frac{a(T - T_c)}{b}} = \frac{c}{2b} \pm \sqrt{\left(\frac{c}{2b}\right)^2 - \frac{(T - T_c)}{T_1}}, \quad (7.5.23)$$

where we have set $T_1 \equiv b/a$, which continues to keep the last term under the square root dimensionless.

The subsequent analysis is a bit tricky. First, note that we must discard the root with the negative sign to guarantee that the order parameter will always remain nonnegative. Second, the sum under the square root must be nonnegative, so as to guarantee that η_0 remains real. In this connection, recall that T_c is the critical temperature encountered by the system when the cubic term is omitted. Thus when $T > T_c$, the largest T value satisfying this requirement is

$$T_m = T_c + T_1 \left(\frac{c}{2b} \right)^2. \quad (7.5.24)$$

This alerts us to the fact that above or at T_m the only physically acceptable solution is $\eta_0 = 0$, while below T_m the solution is specified by Eq. (7.5.23); thus T_m is the actual, transition temperature, which is not an independent variable, as Eq. (7.5.24) shows.

We first note that there is no discontinuity in η_0 or \mathcal{L} at T_c . For this purpose, expand the square root in Eq. (7.5.23) to terms of first order, to find that in the vicinity of T_c

$$\eta_0 = \frac{c}{b} \pm (T_c - T) \frac{a}{c} \quad \text{for } T(\langle or \rangle) T_c; \quad (7.5.25)$$

that is, η_0 smoothly crosses $\eta_0(T_c) = c/b$ and diminishes with rising T . In contrast, we rewrite Eq. (7.5.23) in the format

$$\eta_0(T) = \frac{c}{2b} \pm \sqrt{\left(\frac{c}{2b} \right)^2 - \frac{a[(T - T_m) + (T_m - T_c)]}{b}} = \frac{c}{2b} \pm \sqrt{(T_m - T) \frac{a}{b}}, \quad (T \leq T_m), \quad (7.5.26)$$

which demonstrates again that for $T \geq T_m$, we must employ the solution $\eta_0 = 0$, while for $T < T_m$ the positive root, $\eta_0(T) > 0$ applies. Thus the transition actually occurs at $T_m (> T_c)$, with $\eta_0(T_m) = c/2b$ at a temperature higher than in the absence of the cubic term. The only manifestation of the T_c term is in the sign reversal of term (I), which accelerates the decline of \mathcal{L} with diminishing temperature, and in the specification of T_m , Eq. (7.5.24).

SUMMARY

The Landau approach represents a very compact approach to the general theory of phase transitions, of which the above is a sampling. Further ramifications can be explored by adopting different power series to express \mathcal{L} in terms of η . The flexibility of the Landau theory is certainly impressive. However, it is subject to limitations common to all mean-field theories: the expansion of \mathcal{L} in a limited power series in η and the failure to deal with fluctuation effects.

Reference

- 7.5.1.** N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group* (Perseus Books, Reading, MA, 1992), pp. 141ff.

Correlation Effects: The Ginzburg–Landau Methodology

Here we extend the Landau formalism to deal with correlation functions. We establish these based on a system, the energy states of which are specified by $E_i - X_i Y$. Here, X_i is the response of material in state i to the imposition of an external constraint Y ; earlier we had introduced spins S_i that we presently identify with X_i ; and a magnetic field \mathcal{H} , which corresponds to Y . We next introduce the corresponding partition function (here $\beta \equiv (k_B T)^{-1}$)

$$Z = \sum_i \exp[-\beta(E_i - X_i Y)]; \quad (7.5.27a)$$

and carry out the following operation

$$\left(\frac{1}{\beta} \frac{\partial \ln Z}{\partial Y} \right)_{Y=0} = \left(\frac{1}{\beta Z} \frac{\partial}{\partial Y} \sum_i e^{-\beta(E_i - X_i Y)} \right)_{Y=0} = \left(\frac{1}{Z} \sum_i X_i e^{-\beta(E_i - X_i Y)} \right)_{Y=0} = \langle X \rangle. \quad (7.5.27b)$$

Note that $-(1/\beta) \ln Z = F$, where F is the Helmholtz function; it follows that the mean value of X may be specified via

$$\langle X \rangle = - \left(\frac{\partial F}{\partial Y} \right)_{Y=0}, \quad (7.5.28)$$

Eq. (7.5.27b) provides an alternative approach to the standard method of determining $\langle X \rangle$. Even if no external fields are involved, it may be expedient to introduce a fictitious field Y that we later abandon by setting $Y=0$. Also, on carrying out a second differentiation, we obtain

$$\left(\frac{1}{\beta} \frac{\partial \langle X \rangle}{\partial Y} \right)_{Y=0} \equiv \frac{\chi_T}{\beta} = \langle X^2 \rangle - \langle X \rangle^2. \quad (7.5.29)$$

This defines χ_T as the *generalized susceptibility*, which is directly related to the *fluctuations* in X . The right-hand side is obtained by standard differentiation of Eq. (7.5.27b).

From here, it is but a small step to obtain the correlation functions. For definiteness, consider again the magnetization $\mathcal{M} = \langle S \rangle = \sum_i S_i \equiv \eta$, as the order parameter and let $B_i = \beta \mathcal{H}_i$ be the reduced magnetic field, which we now allow to depend on the location of lattice site i . From the above, it then follows that

$$\langle S_i \rangle = \left(\frac{1}{Z} \frac{\partial Z}{\partial B_i} \right), \quad (7.5.30a)$$

$$\langle S_i S_j \rangle = \left(\frac{1}{Z} \frac{\partial^2 Z}{\partial B_i \partial B_j} \right) \equiv G_s(i, j), \quad (7.5.30b)$$

$$\langle S_i S_j S_k \rangle = \left(\frac{1}{Z} \frac{\partial^3 Z}{\partial B_i \partial B_j \partial B_k} \right) \equiv G_s(i, j, k), \text{ etc.}, \quad (7.5.30c)$$

where G_s , not to be confused with the Gibbs free energy, is the so-called correlation function. Note that Eq. (7.5.30b) is a disguised form of Eq. (7.5.29), where

$$G_s(i, j) = \beta^{-1} \chi_T(i, j), \quad (7.5.31)$$

thereby tying the susceptibility to correlation effects. Eq. (7.5.31) is an example of the *linear response theory*.

When dealing with continuum variables, the above generalizes as shown to $G_S(i, j) \rightarrow G_S(\vec{x}_i, \vec{x}_j)$; also, in very many cases, correlation functions depend not on the absolute positions in space but only on the distance between them. In that case, one deals with $G_S = G_S(|\vec{x}_i - \vec{x}_j|) \equiv G_S(r) = \langle S(0)S(r) \rangle$

Also of interest are the so-called *connected correlation functions*, defined by

$$G_c(i, j) = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle \rightarrow G_c(r) = \langle S(0)S(r) \rangle - \langle S \rangle^2. \quad (7.5.32)$$

We recall that above T_c , $\langle S \rangle = 0$, where $G_c(r) = G(r)$. Below T_c , G_c measures the deviation of spin fluctuations from the equilibrium alignment.

Explicit Determination of Correlation Functions

We now build on the Landau approach to deal explicitly with correlation effects. Here we follow the exposition by Goldenfeld.¹ The coarse-graining procedure used earlier results in the smoothing of physical variables as one proceeds from the atomic domain to Kadanoff block structures. The enumeration of discrete lattice sites is then replaced by the continuum distance variable r , whereby other physical properties such as the order parameter become functions of \mathbf{r} . Close to criticality, the system contains islands of correlated spins of average extension \mathcal{A} given by the correlation length $\xi(T)$, within which one encounters a magnetization

$$\mathcal{M}_\Lambda(\mathbf{r}) = \frac{1}{N_\Lambda(r)} \sum_{i \in r} \langle S_i \rangle, \quad (7.5.33)$$

where $N_\Lambda(r)$ is the number of spins in block \mathcal{A} , and the summation extends over all spins in that block. In contrast to what happens at the atomic domain, we expect the magnetization to vary fairly smoothly in proceeding from one block to the next. To ensure smoothness, we must insert an extra term into the Landau formalism that penalizes extreme variations or discontinuities in $\mathcal{M}(\mathbf{r})$ —domain walls are energetically very expensive. The simplest analytic variation that achieves this aim is of the form

$$\Delta \mathcal{M}_\Lambda(\mathbf{r}) = \Sigma \Sigma \frac{1}{2} \gamma [(\mathcal{M}_\Lambda(\mathbf{r}) - \mathcal{M}_\Lambda(\mathbf{r} + \mathbf{q})) / \Delta \Lambda]^2, \quad (7.5.34)$$

which is independent of the direction \mathbf{q} to the nearest neighbor block. In the limit where \mathcal{M} varies slowly in space, one may sensibly replace the quantity in brackets by the gradient of \mathcal{M} . As before, we identify the magnetization with the proper order parameter η .

To deal with magnetization effects, we generalize Eq. (5.8.5c) for the specification of the Helmholtz function by letting dA depend on the magnetic field H required to maintain the magnetization \mathcal{M} , which is the order parameter. We also assume constant temperature and volume conditions so that only magnetization effects need be considered while also ignoring the small difference between the Gibbs and Helmholtz functions. This allows us to proceed with the Landau functional.

In the current case the order parameter and all other variables are expected to vary with position \mathbf{r} so that when Eq. (7.5.34) is added to the Landau functional (7.5.6) via the coefficient $\gamma/2$, we must also integrate over the extension of the system to obtain the full contribution to the Landau free energy, namely,

$$\mathcal{L} = \int d^d \mathbf{r}' \left[\left(\frac{\gamma}{2} \right) (\nabla \eta)^2 - \mathcal{H} \eta(\mathbf{r}') + a \eta^2(\mathbf{r}') + b \eta^4(\mathbf{r}') / 2 \right]. \quad (7.5.35)$$

The above must now be optimized to obtain the free energy.

The Correlation Function

Before proceeding, we must take note of the following differentiations that also involve definite integrals

$$\frac{\partial}{\partial \eta(\mathbf{r})} \eta(\vec{\mathbf{r}}') = \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}'), \quad (7.5.36)$$

which is obvious. Further,

$$\frac{\partial}{\partial \eta(\mathbf{r})} \int d^d \vec{\mathbf{r}}' \eta(\vec{\mathbf{r}}') = \int d^d \vec{\mathbf{r}} \frac{\partial \eta(\vec{\mathbf{r}}')}{\partial \eta(\vec{\mathbf{r}})} = \int d^d \vec{\mathbf{r}} \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}') = 1. \quad (7.5.37)$$

Finally,

$$\frac{\partial}{\partial \eta(\mathbf{r})} \int d^d \vec{\mathbf{r}}' \frac{1}{2} [\nabla \eta(\vec{\mathbf{r}}')]^2 = -\nabla^2 \eta(\vec{\mathbf{r}}). \quad (7.5.38)$$

This latter relation may be rationalized by examining the integration by parts of a one-dimensional integral: for a well-behaved function $f(x)$

$$\int_a^b dx f \left(\frac{\partial^2 f}{\partial x^2} \right) = f \left(\frac{\partial f}{\partial x} \right) \Big|_a^b - \int_a^b dx \left(\frac{\partial f}{\partial x} \right)^2. \quad (7.5.39)$$

The first- and second terms on the right represent the one-dimensional counterparts of a $d-1$ dimensional surface integral and of a d dimensional volume integral. The first term vanishes if f or its derivative vanishes at both limits. Then, it is assumed that the $d-1$ dimensional surface integral may be ignored. In comparing Eqs. (7.5.39) with (7.5.38), set $f \propto \eta(x')$, but write out the partial derivative as $\partial/\partial \eta(x)$ and then apply Eq. (7.5.36).

The optimization of Eq. (7.5.35) proceeds according to

$$\partial \mathcal{L} / \partial \eta(\mathbf{r}) = -\gamma \nabla^2 \eta(\vec{\mathbf{r}}) + 2at\eta(\vec{\mathbf{r}}) + 2b\eta^3(\vec{\mathbf{r}}) - \mathcal{H}(\mathbf{r}) = 0. \quad (7.5.40)$$

Notice the absence of the integral sign. To obtain an expression for the magnetic susceptibility $\chi_T(\mathbf{r}-\mathbf{r}')$, carry out the operation $\partial/\partial \mathcal{H}(\mathbf{r}')$ on the abovementioned relation. From the definition for χ_T , Eq. (7.5.11), we obtain

$$[-\gamma \nabla^2 + 2at + 6b\eta^2(\vec{\mathbf{r}})] \chi_T(\vec{\mathbf{r}} - \vec{\mathbf{r}}') = \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}'). \quad (7.5.41)$$

One should note the clever way in which the Dirac delta distribution makes its appearance on the right. In view of Eq. (7.5.31), we obtain the following differential equation for $G_s(\mathbf{r}-\mathbf{r}')$

$$\beta [-\gamma \nabla^2 + 2at + 6b\eta^2(\vec{\mathbf{r}})] G_s(\vec{\mathbf{r}} - \vec{\mathbf{r}}') = \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}'). \quad (7.5.42)$$

Technically, G_s is a Green function, because the right-hand side involves the Dirac delta distribution.

There are now two cases to consider

1. $t \equiv (T - T_c)/T_c > 0$; we are above the critical temperature so that the order parameter η vanishes; then the equation to be solved may be rewritten in the form

$$(-\nabla^2 + \xi_u^{-2})G_s(\vec{r} - \vec{r}') = \left(\frac{k_B T}{\gamma}\right)\delta(\vec{r} - \vec{r}'); \quad \xi_u \equiv \left(\frac{\gamma}{2at}\right)^{1/2}. \quad (7.5.43)$$

2. $t < 0$; we are below the critical temperature so that the solution $\eta = (-at/b)^{1/2}$ holds [see Eq. (7.5.7)]; then,

$$(-\nabla^2 + \xi_l^{-2})G_s(\vec{r} - \vec{r}') = \left(\frac{k_B T}{\gamma}\right)\delta(\vec{r} - \vec{r}'); \quad \xi_l \equiv \left(\frac{-\gamma}{4at}\right)^{1/2}. \quad (7.5.44)$$

Both cases are subsumed in the relation

$$(-\nabla^2 + \xi^{-2})G_s(\vec{r} - \vec{r}') = \left(\frac{k_B T}{\gamma}\right)\delta(\vec{r} - \vec{r}'). \quad (7.5.45)$$

In finding a solution, we may set $\vec{r}' = 0$; also, for the spherically symmetric case, we may introduce the radial polar coordinate system in d dimensions: Eq. (7.5.45) then reads

$$\left[-\frac{1}{r^{d-1}} \frac{\partial}{\partial r} r^{d-1} \frac{\partial}{\partial r} + \xi^{-2} \right] G_s(r) = \frac{k_B T}{\gamma} \delta(r). \quad (7.5.46)$$

Introduce $\rho \equiv r/\xi$ as a scaled variable, and note that the scaled Dirac delta function obeys the relation: $\delta(\xi\rho) = \xi^{-d}\delta(\rho)$. Then the partial differential equation takes the form

$$\left[-\frac{1}{\rho^{d-1}} \frac{\partial}{\partial \rho} \rho^{d-1} \frac{\partial}{\partial \rho} + 1 \right] G_s(\rho) = g\delta(\rho), \quad g \equiv \frac{k_B T}{\gamma} \xi^{2-d}, \quad \xi = \xi(t). \quad (7.5.47)$$

This equation is well known in applied mathematics, the solutions of which involve modified spherical Bessel functions of the third kind. The solution for $d = 1$ differs from those for $d \geq 2$; in the latter case, one distinguishes between two limits

When $T \neq T_c$, $r \gg \xi$:

$$G_s(r) = \frac{\pi^{(1-d)/2}}{2^{(1+d)/2}} \cdot \frac{k_B T}{\gamma} \cdot \frac{1}{\xi^{(d-3)/2}} \cdot \frac{e^{-r/\xi}}{r^{(d-2)/2}}. \quad (7.5.48)$$

One should note the dependence of the correlation function G on distance, dominated by the exponential factor, which, incidentally, shows that ξ is to be interpreted as a correlation length. Also involved is the dependence of the correlation length and position variable on the dimension of the system.

On the other hand, when $T = T_c$, the correlation length $\xi \rightarrow \infty$, and the solution approaches the opposite asymptotic case, $r \ll \xi$: namely, for $d > 2$, (Γ is the standard gamma function)

$$G_s(r) = \frac{\Gamma((d-2)/2)}{4\pi^{d/2}} \cdot \frac{k_B T}{\gamma} \cdot \frac{1}{r^{d-2}}, \quad (7.5.49)$$

where the distance dependence differs from the earlier version: it is strongly dependent on dimension d . Moreover, the power law of this dependence involves integer exponents (since we are not dealing here with fractal dimensions). However, in detailed experimental investigations, one encounters a power decay law of the form

$$G(r) \sim \frac{A}{r^{d-2+\eta}}, \quad (7.5.50)$$

with η (which is standard notation, not to be confused with the order parameter used earlier) in the range 0.016–0.06. This is a small correction but is by no means negligible. To get from the present mean-field theory, where $\eta = 0$, to a theoretical derivation of the experimentally observed η values requires considerable mathematical acrobatics that are beyond our purview.

Summarizing, away from criticality, the correlation function varies as $e^{-r/\xi}/r^{(d-2)/2}$; at the critical temperature, it varies as $1/r^{d-2+\eta}$; both versions are linear in temperature.

Lastly, note that the utility of Eq. (7.5.49) goes far beyond its immediate application in this section: it forms the starting point for excursions into statistical field theories that are employed in constructing contemporary theories of critical phenomena.

Reference

- 7.5.1.** N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group* (Perseus Books, Reading MA, 1992), Chapter 5.

Topics Related to Critical Phenomena

8

Here we briefly engage in a cursory glance at some items related to critical phenomena that did not readily fit in the earlier discussion.

8.1 Homogeneous Functions

We first deal with a brief foray into the concept of *homogeneous functions*. This is a generalization of the obvious fact that quadrupling the area of a square is achieved by doubling the length of its side. We generalize on this concept by introducing a function f of a single variable that is homogeneous in degree n if it satisfies the relation

$$f(\lambda x) = \lambda^n f(x) \quad (8.1.0a)$$

for all λ . In this elementary example, x is the independent variable and λ is a *scaling transformation*. This idea can be further generalized in two ways: homogeneous functions have the property that if a function f is known at one point x_0 then f is known over the whole domain of its validity, via the relation

$$x = \lambda x_0, \text{ or } f(x) = f(\lambda x_0) = \lambda^n f(x_0). \quad (8.1.0b)$$

The above can be extended to any number of independent variables: *Generalized homogeneous functions* of degree n satisfy the relation

$$f(\lambda^r x_1, \lambda^s x_2, \dots) = \lambda^n f(x_1, x_2, \dots) \quad (8.1.1)$$

for all λ . The utility of such functions in the rescaling process has been demonstrated in earlier chapters. Functions other than power laws do not exhibit this property and are therefore not suitable for scaling-up processes, in which the enlarged set replicates the properties of the smaller units. This is one of the distinguishing features of homogeneous functions.

An immediate consequence of the above emerges for the special case of two independent variables in the particular form

$$f(\lambda x, \lambda y) = \lambda^p f(x, y). \quad (8.1.2)$$

By adopting the choice $\lambda = 1/x$ we find that

$$f(1, y/x) = (1/x)^p f(x, y), \quad (8.1.3)$$

or,

$$f(x, y) = x^p f(1, y/x); \quad f(x, y)/x^p = g\left(\frac{y}{x}\right). \quad (8.1.4)$$

Note how the two independent variables shows up as a single ratio on the right.

Fractals

The scaling property referred to above has an interesting visual counterpart, which involves certain geometric structures generated by *fractals* to yield constructs via recursive processes. A fractal is an object that at sufficient magnification displays jagged boundaries that retain the same, or very similar, characteristic features when examined at any magnification—a feature that is known as *self-similarity*. Boundaries of such constructs, while continuous, are so jagged that it is not possible to identify at high resolution a region suitable for the application of standard processes of differentiation.

An elementary illustration of how to generate such objects by iterative processes is furnished by the so-called Koch curve (von Koch, 1904). As shown in Figure 8.1.1, $n = 0$, the starting point is the equilateral triangle. In the first iteration, each side is divided into three segments, the central portion is replaced as shown in Figure 8.1.2, and the resulting construct replaces each side of the original triangle, as shown for the case $n = 1$. This process is then repeated: every straight line segment of the $n = 1$ figure is replaced by the Figure 8.1.2 configuration to generate the $n = 2$ structure. Jaggedness emerges at the $n = 5$ stage and thereafter becomes increasingly prominent. The Koch curve is a primitive example of a fractal.

A more sophisticated construct is the so-called Sierpinski gasket shown in Figure 8.1.3, generated by inserting a set of inverted equilateral triangle into a noninverted one, thereby generating small upright triangles. This process can be continued indefinitely at all length scales, though of course we are limited by the finite size of our drawing instruments. There is an entire industry for generating such interesting structures, of which the above are among the two best known.

Algebraic Power Laws and Fixed Critical Points

Here we reexamine briefly the use of algebraic power laws; these are far more ubiquitous in science than is suggested by their earlier use in our discussion of critical phenomena. They turn up in the handling of random phenomena, and are thus quite distinct from the orderly treatment of ensemble averages prevailing at equilibrium. A large class of nonequilibrium phenomena falls into this category. Some of these spontaneously evolve into distinct classes of critical states without any external prodding, a property that comes under the designation of *self-organized criticality*. Phenomena in the category that display power law distributions include the Pareto distribution of wealth in our society, the number of earthquakes releasing energies within a certain range, the distribution of towns with a specified population range, the distribution of words of different lengths in a language. Or: the occurrence of volcanic eruptions, forest fires, traffic congestion, scientific citations—as a sampling of disparate events characterized by power laws. None of these phenomena can be assigned an average value because they are randomly scale invariant. For a given process the underlying mechanism is the same whether its manifestation involves large or small changes: while huge earthquakes have enormous consequences relative to small tremors, fundamentally they are not exceptional.

The classification of the above events by a simple power law should give one pause. It is not at all clear why the analysis of the complexities involved in any of the above events should be reducible to a simple algebraic relation.

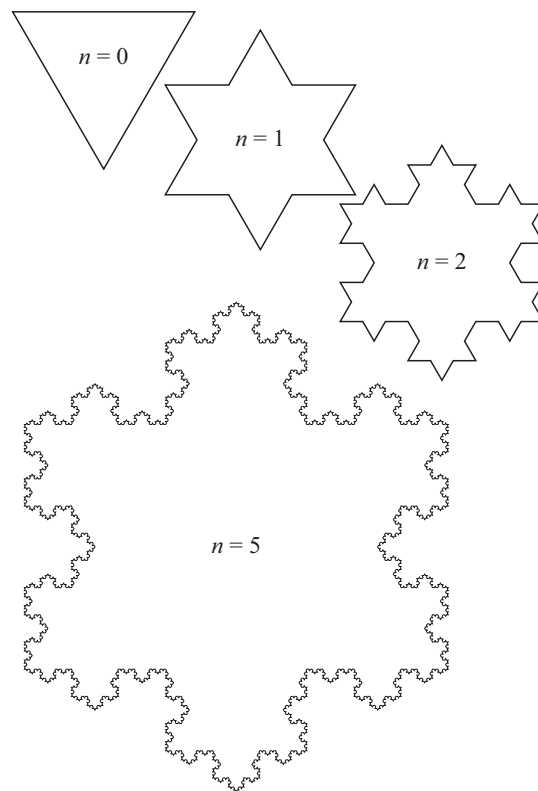


FIGURE 8.1.1

Illustration of the process of generating the Koch curve.

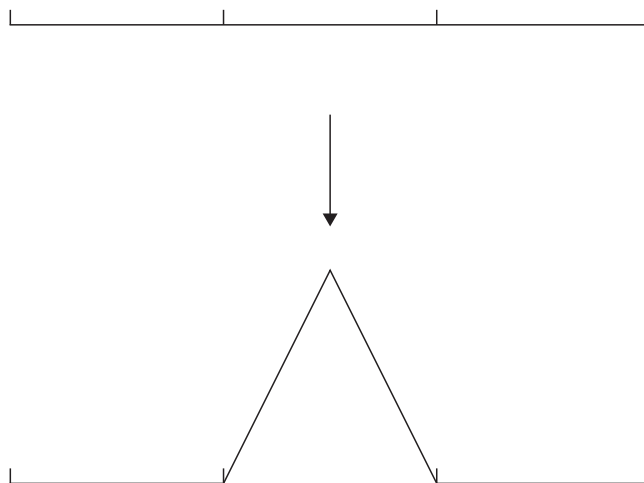


FIGURE 8.1.2

The implementation of the first iteration for generating the Koch curve.

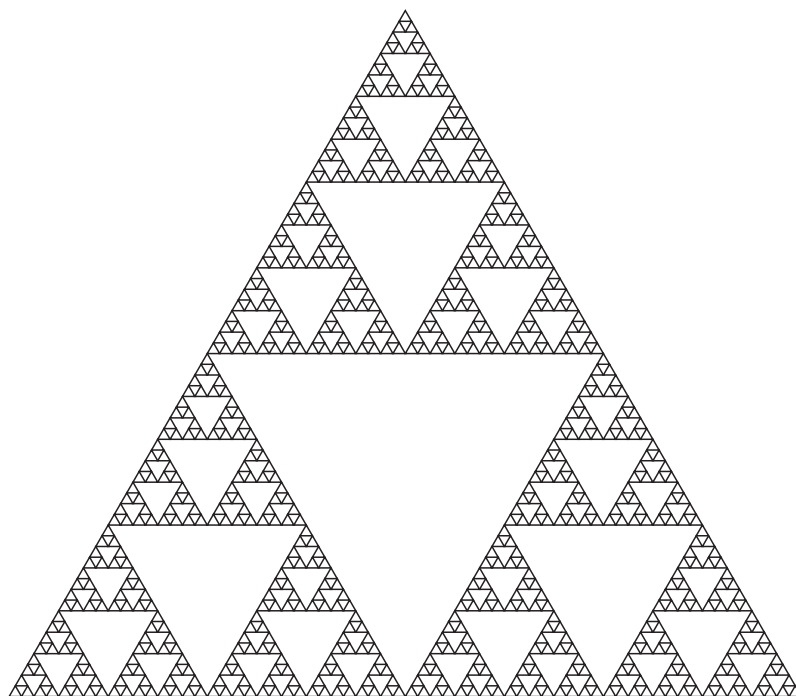


FIGURE 8.1.3

The Sierpinski gasket generated from a set of inverted equilateral triangles inserted in an upright equilateral triangle.

8.2 Fixed Points

As another item of discussion, we illustrate the idea of a fixed point by considering an equation of the form

$$X(n + 1) = f(X(n)). \quad (8.2.1)$$

This is a recursive relation that shows how to proceed from the n th stage to the next once you specify the function f . This is quite distinct from most of the phenomena treated in this book, whereby changes in properties are treated via a sum of minute alterations in properties of the constituents. The above recursion process leads to a *fixed point* if there exists a constant $X(0) = c$ such that for all n the requirement $X(n) = c$ is met. Stated differently, the quantity c is a fixed point of Eq. (8.2.1) if and only if $c = f(c)$. Thus the recursive process of Eq. (8.2.1) may or may not lead to a specific, invariant end point. This matter is illustrated next.

8.3 Remarks Concerning Chaos Theory

As a conclusion to the present book let me—perhaps aptly—engage in a very cursory foray into the general approach to Chaos theory, which is the very opposite of the orderly treatment of physical phenomena afforded by classical thermodynamics. This approach is perhaps best illustrated via two specific examples.

The Logistic Map

Consider the following innocent-looking equation, termed a *logistic map*

$$x_{n+1} = rx_n(1 - x_n), \quad (8.3.1)$$

which is not just a mathematical curiosity but finds numerous applications, among them the control of population levels, or the stimulated emission of laser pulses. It relates via a growth parameter r the value of the independent quantity x at the n th iteration to its value at the next iteration. This difference equation should be sharply contrasted with the differential equations forming the backbone of thermodynamics.

The implications involved in the use of Eq. (8.3.1) are best explored in terms of diagrams that feature plots of the parabolic $rx(1 - x)$ function as well as the linear rise for r values in the range $0 \leq x \leq 1$

Matters start out simply: Figure 8.3.1 shows the plots for both the above functions, setting $r = 1.50$, and starting with $x_0 = 0.05$ as the input value. The vertical bars on the staircase pattern displays the iterates: $x_1 = 0.071\dots$, $x_2 = 0.099\dots$, $x_3 = \dots$, up to the intersection point at $x_\infty = 0.333\dots$, which remains fixed, no matter how many additional iterations are performed. We have arrived at a specific end point.

Figure 8.3.2 is more interesting: with $r = 2.50$ and starting again at $x_0 = 0.05$ we once more get the staircase effect, but close to the end point the graph oscillates between two distinct values in the range $x_l = 0.599\dots$ and $x_u = 0.626\dots$ before shrinking in size, and ultimately settling in on $x_\infty = 0.600$ again, a fixed point, but one reached via detours.

Things get even more interesting as we go on. Figure 8.3.3 shows a mapping with $r = 3.20$ and an input parameter $x_0 = 0.23$ (allowing us to concentrate on the important part of the map). We ultimately encounter endless oscillations between the values $x_l = 0.513\dots$ and $x_u = 0.799\dots$. No fixed end point is reached. This situation is said to constitute a *bifurcation*.

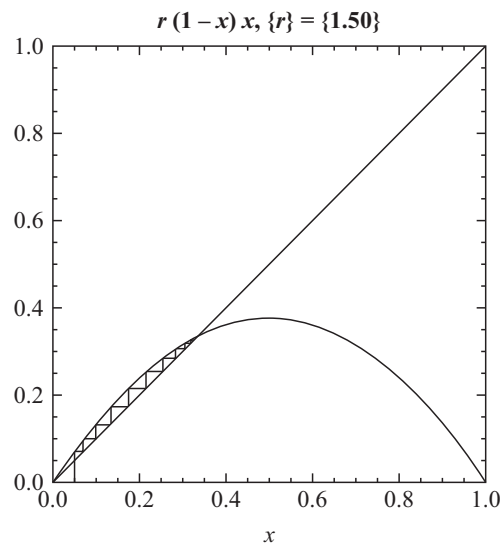


FIGURE 8.3.1

Display of the logistics map for $r = 1.50$. Note the progression from the initial input parameter $x_0 = 0.05$ to the final value at $x = 0.333$.

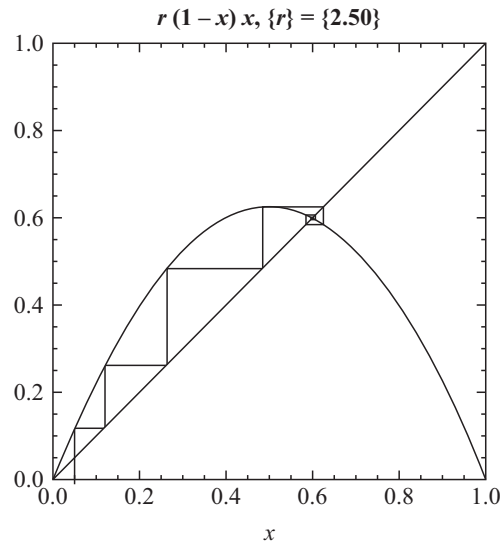


FIGURE 8.3.2

Display of the logistics map for $r = 2.50$. Note the progression from the initial input parameter $x_0 = 0.05$ to the final value at $x = 0.600$.

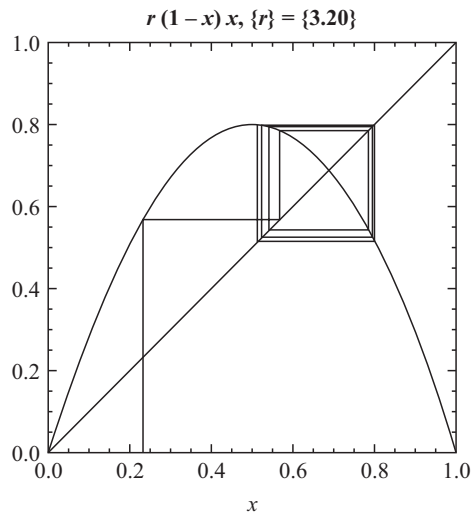


FIGURE 8.3.3

Display of the logistics map for $r = 3.20$; with the input parameter $x_0 = 0.23$.

Somewhat similar results are displayed for $r = 3.50$, $x_0 = 0.23$. Figure 8.3.4(a) shows the erratic approach of the iterates to a final set of results. Figure 8.3.4(b) displays the end results after discarding all the cobwebby approaches to the so-called period four orbits, at $x = 0.382\dots, 0.500\dots, 0.826\dots, 0.874\dots$. Eight orbit figures are encountered for $r = 3.55$, as shown in Figure 8.3.5. This orbit doubling process continues until the limit $r = 3.569\dots$ is reached.

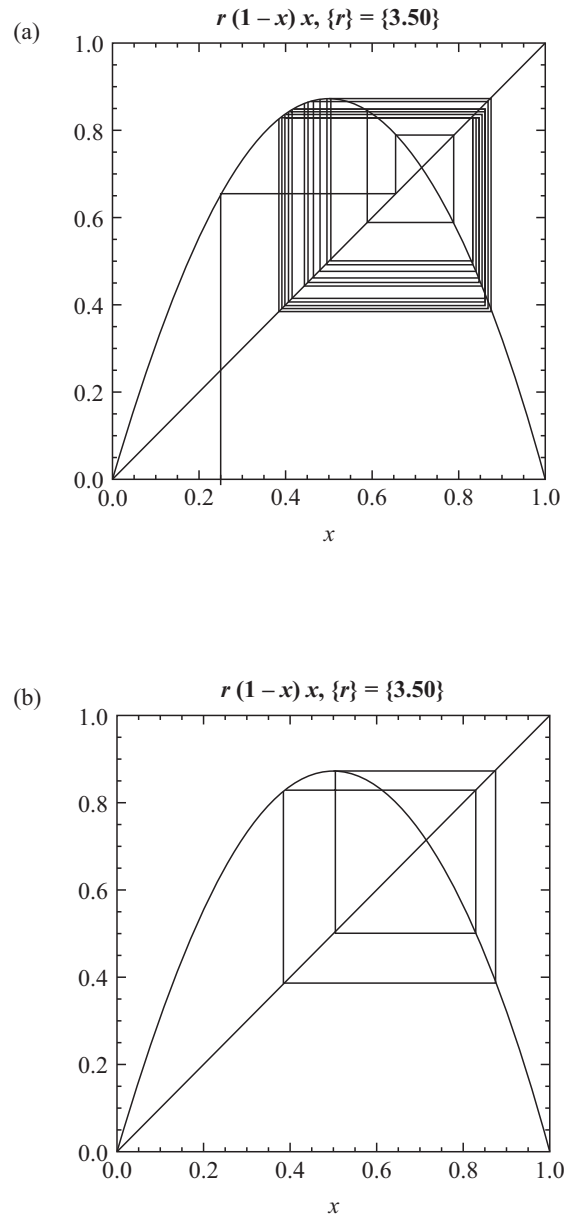


FIGURE 8.3.4

(a) Display of the logistics map for $r = 3.50$; with the input parameter $x_0 = 0.23$. (b) Display of the logistics map for $r = 3.50$; with the input parameter $x_0 = 0.23$; for clarity the progression from x_0 to the final four orbits has been deleted.

An entirely new situation emerges for larger r values, where one encounters a denumerably infinite set of solutions. This is verified by examining an arbitrarily chosen set of 50 iterates of x against the time at which the iterate was examined. The results are shown in Figure 8.3.6 for $r = 3.70$. While the readings fall in the range $0.26 \leq x \leq 0.92$ there is no predictable, let alone unique, set of x values; also,

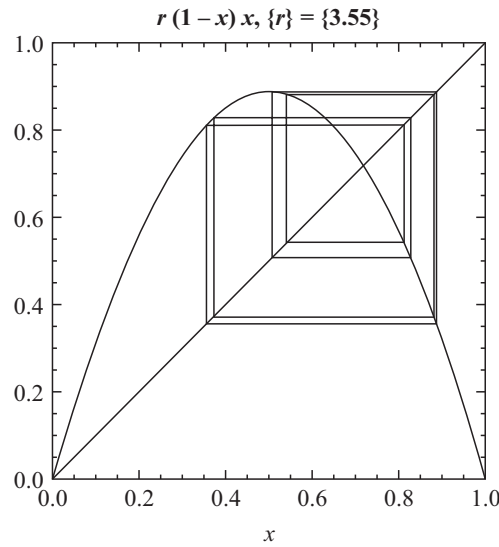


FIGURE 8.3.5

Display of the logistics map for $r = 3.55$; with the input parameter $x_0 = 0.25$. For clarity the progression from x_0 to the final eight orbits has been deleted.

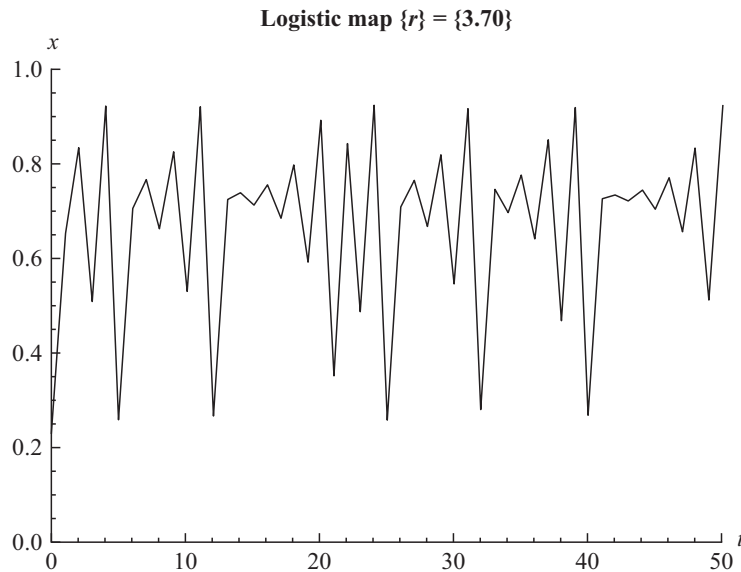


FIGURE 8.3.6

Display of 50 successive x readings resulting from the logistics map with $r = 3.70$. Note the chaotic alterations of x readings generated by the deterministic Eq. (8.3.1).

no truly repetitive patterns can be discerned. In other words, we are totally ignorant of what x value is going to emerge from the wealth of possible solution of the deterministic Eq. (8.3.1) under this set of parameters. We have reached the *chaotic state*.

A neat summary of the results is depicted in Figure 8.3.7, exhibiting a plot of x versus r . It is a good exercise to match the earlier plots with their location on this diagram. The onset of bifurcation is

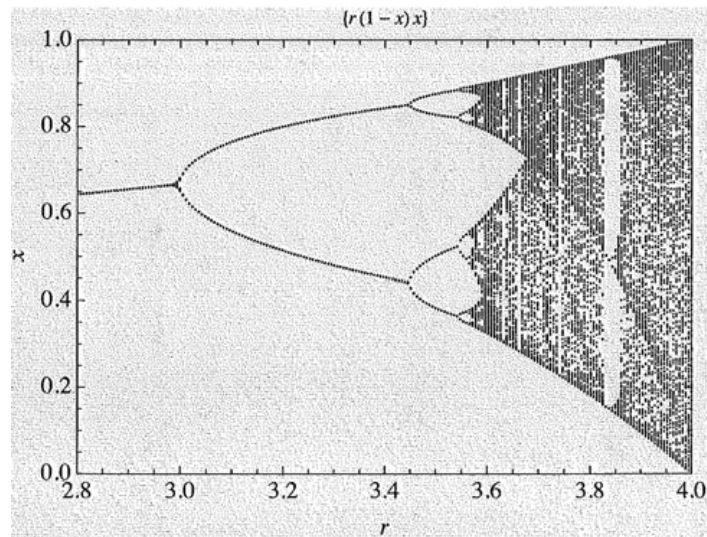


FIGURE 8.3.7

Display of the variation of x versus r for the logistics map in the range $2.8 \leq r \leq 4.0$.

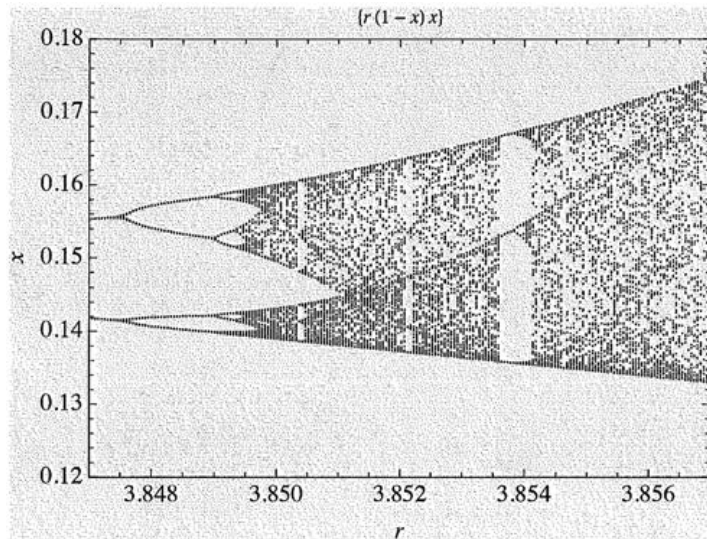


FIGURE 8.3.8

Display of the variation of x versus r for the logistics map in the range $3.847 \leq r \leq 3.857$.

clearly in evidence at $r = 3$, as is the emergence of additional bifurcations in the range $3.4 < r < 3.57$. Chaos sets in at $r \approx 3.57$, beyond which any value of x within the indicated limits is encountered. The emergence of small blank patches indicates regions where no solution exists. One should also recognize the obvious feature just beyond $r = 3.83$, where the system once more settles down to a three- or four-orbit state. The resultant structure is detailed in Figure 8.3.8; one should note the scale changes relative to Figure 8.3.7. Beyond this point the chaotic state resumes.

The Stiff Pendulum

As an entirely different illustration of the emergence of chaos we briefly follow the discussion provided by M. Longair,¹ relating to the motion executed by a stiff pendulum. The relevant equations of motion read as follows:

$$\frac{d\omega}{dt} = -(1/q)\omega - \sin\theta + \alpha\cos\varphi \quad (8.3.2)$$

$$\frac{d\theta}{dt} = \omega \quad (8.3.3)$$

$$\frac{d\varphi}{dt} = \omega_D. \quad (8.3.4)$$

where ω is the instantaneous angular velocity, θ is the angle of the pendulum with respect to the vertical, φ is the phase of the driving force operating at fixed angular frequency ω_D , α an adjustable parameter, and q , the quality factor.

The resulting trajectories, as determined by numerical solution of Eqs. (8.3.2)–(8.3.4) are presented as plots of ω versus θ for several choices of (q, α) at a fixed value of ω_D ; where possible the trajectories in real space are also shown. That Eqs. (8.3.2)–(8.3.4) are indeed the relevant equations for a pendulum is indicated by the first display, Figure 8.3.9(a), which for $(q = 2, \alpha = 0.5)$ shows the anticipated regular behavior. For $q = 2, \alpha = 1.07$, Figure 8.3.9(b), the earlier, simple ellipse becomes distorted, indicative of the more complex trajectory shown on the left. For the indicated phase diagrams of Figure 8.3.9(c) and (d), the open ends should be joined to complete the loops. As shown, with increasing values of α greater deviations from the normal pattern become manifest. There is, however, no steady progression in this pattern: in Figure 8.3.10 are shown two cases $(q = 2, \alpha = 1.15, 1.50)$, where chaos reemerges. It is remarkable that the above differential relations generate features rather similar to the recursive configuration encountered in the logistics map.

Many other cases of this type are encountered in the literature. It is well worth pondering the implications of starting off with deterministic equations that end up with unpredictable outcomes.

Appendix: The Role of Fisher Information Theory in the Development of Physical Laws

This section represents an elementary introduction to what might be called *the thermodynamics of information theory*, as developed by Fisher.² This is one of the truly fundamental approaches to scientific methodology, in the sense that, in conjunction with appropriate constraints, a large number of different physical laws can be derived from a common source in a unified manner. A more rigorous, informative, and extensive presentation may be found in a monograph by Roy Frieden.³

Basics

The theory rests on measurements of a physical variable, such as position, y , of a fundamental particle. The very act of observation interferes with the measurement, which therefore ordinarily does not coincide with the value θ of the actual position. Denote by x_n , which may be positive or negative, the deviation of the n th measurement from the actual value, so that

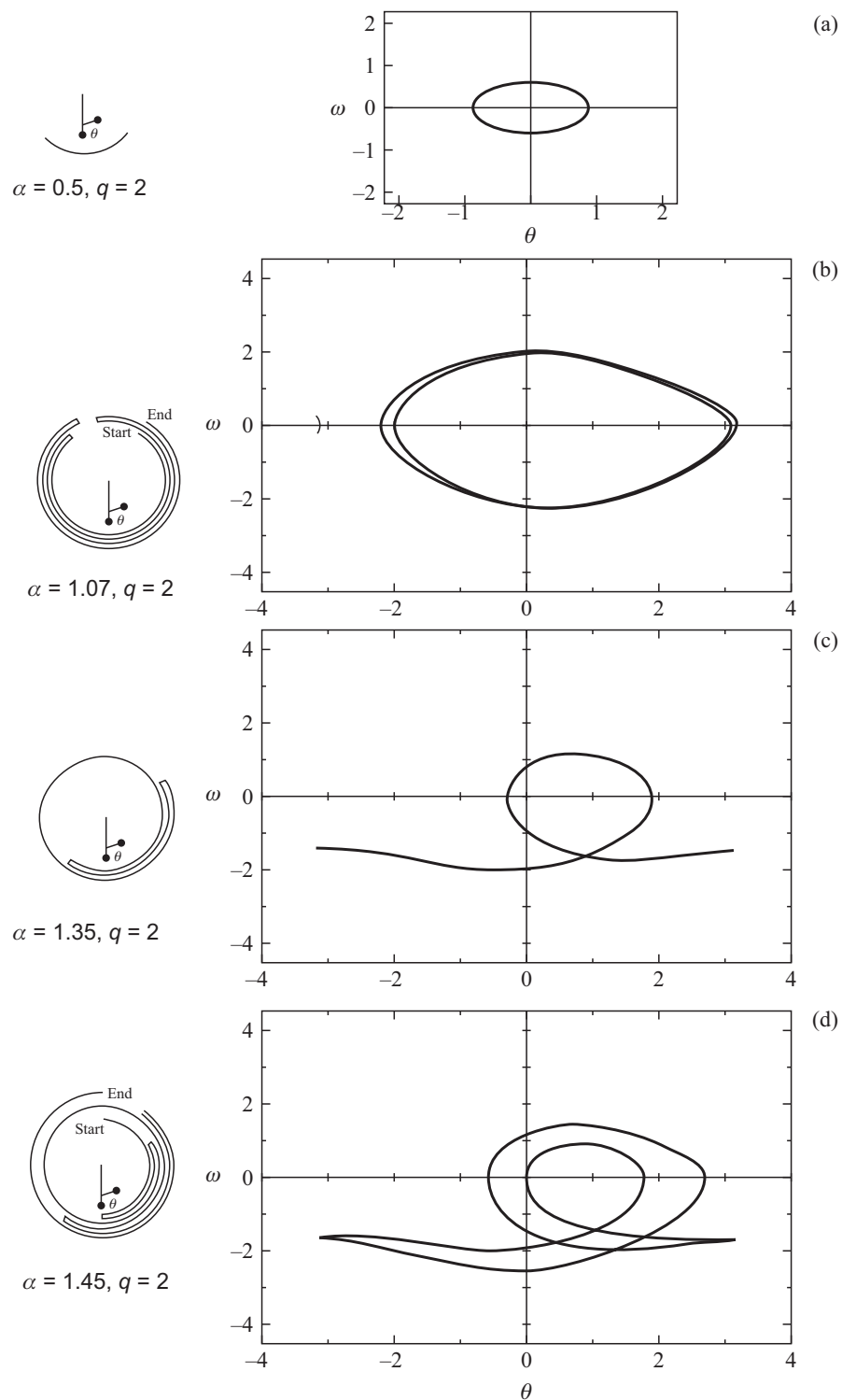


FIGURE 8.3.9

Trajectories and phase diagrams of the stiff pendulum resulting from Eqs. (8.3.2)–(8.3.4) for the indicated parameters.

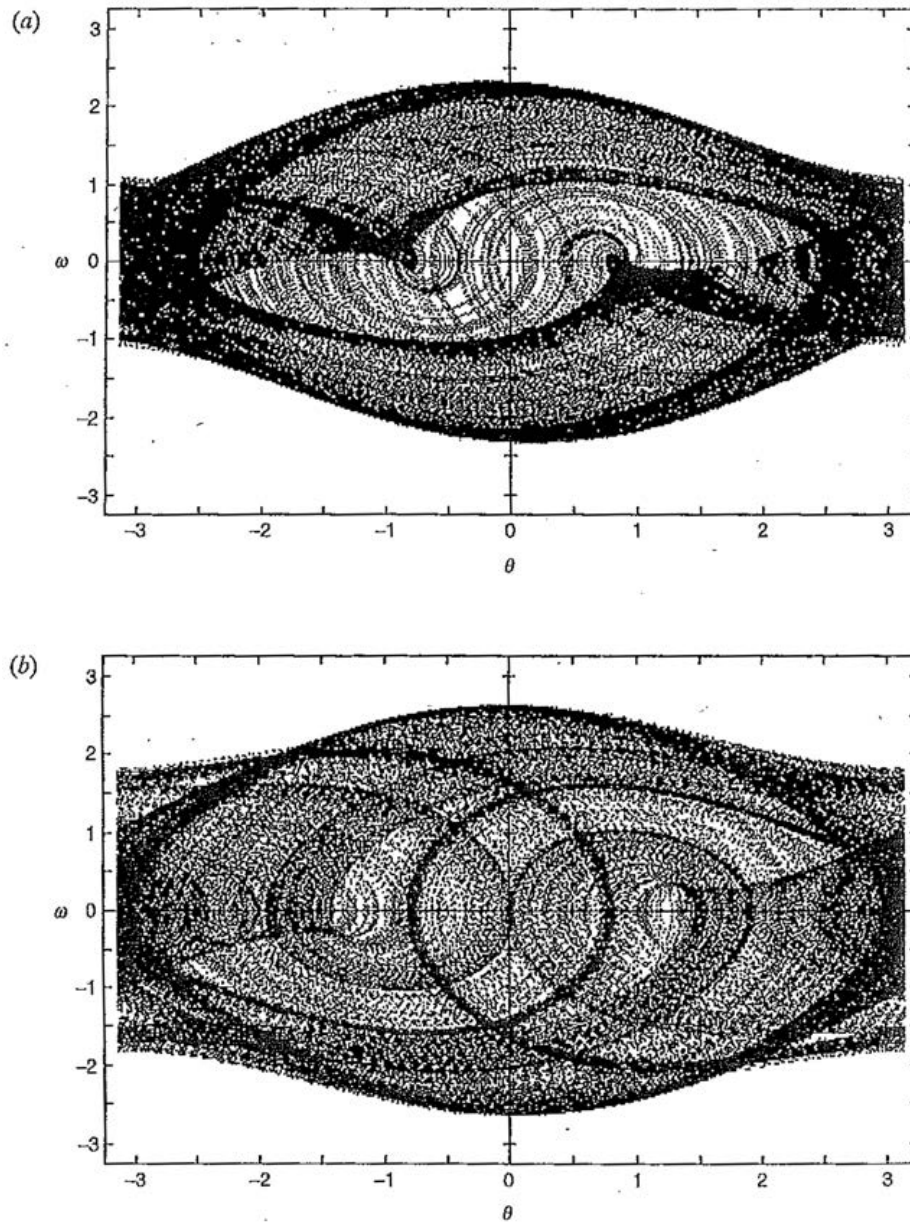


FIGURE 8.3.10

Phase diagrams displaying chaotic properties associated with the deterministic differential Eqs. (8.3.2)–(8.3.4), for $q=2$ and $\alpha = 1.15$ (a); $\alpha = 1.50$ (b).

$$y_n = \theta + x_n \quad (8.3.5a)$$

These measurements result in an optimized value $\hat{\theta}$, obtained by averaging over N repetitions of the experimental measurements. The resulting mean value

$$\hat{\theta} = \hat{\theta}(\mathbf{y}) = N^{-1} \sum_n y_n \quad (8.3.5b)$$

usually provides a better approximation to θ than does a single measurement. In unbiased measurements the best estimate is attained by minimizing the mean square error, specified by

$$e_y^2 \equiv \left\langle \left[\hat{\theta}(\mathbf{y}) - \theta \right]^2 \right\rangle, \quad (8.3.6)$$

where angular brackets denote expectation values. However, as already stated, and is also demonstrated later, there will always remain an irreducible difference between $\hat{\theta}$ and θ .

We illustrate the above statements by considering a box containing one atom, surrounded by a tangle of heating wires that generates a very uneven temperature profile within the box. On completion of one set of measurements the experimental conditions may be altered by changing the configuration of the heating wires. This represents one way of realizing the partial differentiation with respect to θ called for in Eq. (8.3.8) is displayed below. To determine θ under a set of specified conditions an experimentalist takes (perhaps not literally) N successive snapshots of the atom, to calculate the average value, $\hat{\theta}(\mathbf{y}) = N^{-1} \sum_n y_n$, over all measurements of the atomic positions y_n in the various snapshots. The notation $\hat{\theta}(\mathbf{y}), \mathbf{y} = \{y_n\}$ implies that the averaging changes with the particular sequence of the N measurements adopted in any one identical set of measurements.

Let p represent the probability that a value \mathbf{y} is encountered for the position of the particle in an ensemble for which the actual value is θ . The expectation value of the deviation from the correct value is given by

$$\left\langle \left[\hat{\theta}(\mathbf{y}) - \theta \right] \right\rangle = \int_{-\infty}^{\infty} d\mathbf{y} p(\theta, \mathbf{y}) \left[\hat{\theta}(\mathbf{y}) - \theta \right] = 0. \quad (8.3.7)$$

Eq. (8.3.7) does not contradict (8.3.6) since deviations of $\hat{\theta}(\mathbf{y})$ from θ may be negative as well as positive.

Now differentiate with respect to θ ; for fixed integrals one may execute this step under the integral sign

$$\frac{\partial}{\partial \theta} \int_{-\infty}^{\infty} d\mathbf{y} p(\theta, \mathbf{y}) \left[\hat{\theta}(\mathbf{y}) - \theta \right] = \int_{-\infty}^{\infty} d\mathbf{y} \frac{\partial p(\theta, \mathbf{y})}{\partial \theta} \left[\hat{\theta}(\mathbf{y}) - \theta \right] - \int_{-\infty}^{\infty} d\mathbf{y} p(\theta, \mathbf{y}) = 0. \quad (8.3.8)$$

The second integral converges to unity because the probabilities are normalized. Also, we set

$$\frac{\partial p(\theta, \mathbf{y})}{\partial \theta} \equiv \frac{\partial \ln p(\theta, \mathbf{y})}{\partial \theta} p(\theta, \mathbf{y}), \quad (8.3.9)$$

whence, Eq. (8.3.8) may be rewritten as

$$\int_{-\infty}^{\infty} d\mathbf{y} \frac{\partial \ln p(\theta, \mathbf{y})}{\partial \theta} p(\theta, \mathbf{y}) [\widehat{\theta}(\mathbf{y}) - \theta] = 1. \quad (8.3.10)$$

Square the above equation:

$$L \equiv \left\{ \int_{-\infty}^{\infty} d\mathbf{y} \left(\frac{\partial \ln p(\theta, \mathbf{y})}{\partial \theta} \sqrt{p(\theta, \mathbf{y})} \right) [\sqrt{p(\theta, \mathbf{y})}] [\widehat{\theta}(\mathbf{y}) - \theta] \right\}^2 = 1. \quad (8.3.11)$$

Next, invoke Schwarz' inequality, which for two complex functions $f(x)$ and $g(x)$ (asterisks denote complex conjugates) states that

$$\left| \left[\int_a^b d\mathbf{y} f(x) g(x) \right] \right|^2 \leq \int_a^b f^*(x) f(x) dx \cdot \int_a^b g^*(x) g(x) dx. \quad (8.3.12)$$

When f and g are real functions, Eq. (8.3.12) as applied to (8.3.11) yields

$$L = 1 \leq \int_{-\infty}^{\infty} d\mathbf{y} \left(\frac{\partial \ln p(\theta, \mathbf{y})}{\partial \theta} \sqrt{p(\theta, \mathbf{y})} \right)^2 \cdot \int_{-\infty}^{\infty} d\mathbf{y} [p(\theta, \mathbf{y})] [\widehat{\theta}(\mathbf{y}) - \theta]^2. \quad (8.3.13)$$

In most cases of interest the probabilities obey the “shift relation”

$$p(\theta, \mathbf{y}) = p(\mathbf{y} - \theta) \equiv p(\mathbf{x}). \quad (8.3.14)$$

Then, the first integral in L , Eq. (8.3.13), is defined to be the *Fisher Information Measure*, I : thus, in terms of the shift

$$I \equiv \int_{-\infty}^{\infty} d\mathbf{y} \left(\frac{\partial \ln p(\mathbf{y} - \theta)}{\partial \theta} \right)^2 p(\mathbf{y} - \theta). \quad (8.3.15)$$

The second integral is defined to be the *Mean Squared Error*, e_y^2 for measurements of an ensemble of particles:

$$e_y^2 \equiv \int_{-\infty}^{\infty} d\mathbf{y} [p(\mathbf{y} - \theta)] [\widehat{\theta}(\mathbf{y}) - \theta]^2, \quad (8.3.16)$$

which agrees with the definition (8.3.6). Clearly, as applied to the position \mathbf{y} of the particle, e_y^2 determines in repeated measurements the square of the fluctuations from its actual position; hence, e_y relates to the uncertainty in our knowledge of its exact position. Henceforth, we restrict ourselves to the one-dimensional case.

Now set $x = y - \theta$, $(\partial/\partial x) \left(\frac{\partial x}{\partial \theta} \right) = -(\partial/\partial x)$, so that Eq. (8.3.15) reads

$$I = \int_{-\infty}^{\infty} dx \left(\frac{1}{p(x)} \frac{\partial p(x)}{\partial x} \right)^2 p(x) = \int_{-\infty}^{\infty} dx \left(\frac{\partial p(x)}{\partial x} \right)^2 \frac{1}{p(x)}. \quad (8.3.17)$$

Continuing now with the main argument, on applying (8.3.15) and (8.3.16) to (8.3.13) one obtains the so-called *Cramer–Rao* inequality:

$$1 = L \leq e_y^2 I, \text{ or } e_y^2 \geq \frac{1}{I}. \quad (8.3.18)$$

Obviously, for real y , I is a positive number. Thus, the above equation sets a lower nontrivial bound on the mean square error or uncertainty in *any measurement*. This has obvious repercussions in formulating the Heisenberg inequality in quantum mechanics but also refers to inevitable errors in the physical measurement of any observable quantity. When the equality obtains one faces an irreducible minimum in the measurement errors.

Two limiting cases are worth noting: (1) The first relates to deviations from the correct value for which the distribution p is “flat”: Here the measurements are more or less uniformly distributed over the entire interval $-\infty < x < \infty$. Then $dp/dx \approx 0$, $I \rightarrow 0$, and e_y^2 is essentially unbounded: a broad and smooth distribution implies considerable randomness and a large mean square error. (2) $p(x)$ peaks sharply about y_0 . Now $(dp/dy)^2$ is large near y_0 but close to zero elsewhere. I grows larger and e_y^2 smaller the more peaked the distribution becomes, corresponding to a smaller degree of randomness. Thus I is in fact a measure of the disorder of a system. This leads to the association of I with the negentropy, generally defined as $H \equiv -\int dy p(y) \ln p(y)$ [H is not the eighth letter of the Latin alphabet, but cap Greek “eta”]; this relationship can be properly established through discussions beyond the present purview.

Since I relates to negentropy it follows that $dI/dt \leq 0$; that is, in *any process* under consideration I diminishes and tends toward a minimum, at which $\delta I = 0$. The special circumstances that characterize the processes occurring in a particular system are introduced via constraints, such as requiring all distribution functions to be normalized, requiring the energy of an isolated system to be fixed, or more generally, introducing constraints of the type discussed in Ref. 3. It follows further that the mean square error grows as the Fisher information diminishes with increasing time. That is, random processes that are inevitable in any physical measurements become increasingly more severe. However, when the constraints are applied, as shown later, $p(x)$ approaches a constant, lower limit, that is, a stationary state—in which I assumes its minimum value. This is the essence of the *Extreme Fisher Information Principle*, which is at the heart of the derivations described in the literature.

The detailed applications of this general approach to a large variety of special cases are beyond the purview of the present introduction but are described in detail in Ref. 3. Here we consider a few specific examples that represent the approach used in all applications, beginning with the derivation of the one-dimensional Schrödinger equation.

The Schrödinger Equation

Consider again the problem of locating a particle anywhere within a one-dimensional region. In the absence of any constraints the particle could be anywhere with equal probability. As mentioned previously, this translates into the requirement that the Fisher information should be at an extremum. However, since the particle is subjected to an external, specified potential $V(x)$, the probability of locating the particle will be influenced thereby. Relative to the unknown total energy E the mean kinetic energy of the particle, $\langle K \rangle$, which is positive, is subject to the constraint

$$\langle K \rangle = \int_{-\infty}^{\infty} dx p(x) [E - V(x)] > 0. \quad (8.3.19)$$

This constraint is handled in a manner analogous to the method of Lagrangian multipliers: Instead of minimizing I one minimizes the augmented function

$$\int_{-\infty}^{\infty} dx \left(\frac{dp(x)}{dx} \right)^2 \frac{1}{p(x)} + \lambda_0 \int_{-\infty}^{\infty} dx [E - V(x)] p(x) = \text{extrem.} \quad (8.3.20)$$

where λ_0 is an undetermined multiplier.

It is convenient at this stage to introduce a *probability amplitude* $q(x)$, defined by

$$p(x) = |q(x)|^2, \quad (8.3.21)$$

The integral I now reads

$$I = \int_{-\infty}^{\infty} dx \left(2q(x) \frac{dq(x)}{dx} \right)^2 \frac{1}{q^2(x)} = 4 \int_{-\infty}^{\infty} dx \left(\frac{dq(x)}{dx} \right)^2. \quad (8.3.22)$$

whereby Eq. (8.3.20) is rewritten as ($\lambda = \lambda_0/4$)

$$L = \int_{-\infty}^{\infty} dx \left(\frac{dq(x)}{dx} \right)^2 + \lambda \int_{-\infty}^{\infty} dx [E - V(x)] |q(x)|^2 = \text{extrem.} \quad (8.3.23)$$

As is well established one handles the extremum problem by solving the (nontemporal) *Euler-Lagrange Equation*.

$$\frac{d}{dx} \left(\frac{\partial L}{\partial q'} \right) - \frac{dL}{dq} = 0; \quad L = q'^2 + \lambda q^2 [E - V(x)]; \quad q' \equiv \frac{dq}{dx}. \quad (8.3.24)$$

At this stage it is vital, for purposes of proper treatment, to regard the symbols q and q' as unrelated quantities. Straightforward solution of the extremal equation yields

$$\frac{1}{\lambda} \frac{d^2 q}{dx^2} - q [E - V(x)] = 0. \quad (8.3.25)$$

This is seen to be a disguised form of the Schrödinger equation; in usual notation q is replaced by ψ and λ , by $-(\hbar^2/2m)^{-1}$.

Aside from the obvious *tour de force* one should note how the second derivative has entered Eqs. (8.3.15) and (8.3.7) through use of the Fisher information function I . The presence of this derivative in the conventional presentation of Schrödinger's equation has always been considered as somewhat of a puzzle; one generally simply posits that the classical momentum should be replaced by the operator $-i\hbar d/dx$. Here the second derivative occurs in a natural setting without requiring *ad hoc* arguments. In a sense the Schrödinger equation is simply a consequence of minimizing the Fisher information.

The Maxwell Boltzmann Distribution Law

We go back to Eq. (8.3.13) and now apply the ordinary equipartition law to the expectation value of the kinetic energy of particles at temperature T moving in one dimension:

$$\langle K \rangle = \int dx \left(\frac{mx^2}{2} \right) p(x) = \frac{kT}{2}. \quad (8.3.26)$$

This represents one constraint that is relevant to our discussion. A second is the normalization for the probabilities of encountering gas molecules in the domain $-\infty < x < \infty$, as specified by

$$\int dx p(x) = 1. \quad (8.3.27)$$

On applying the method of undetermined Lagrangian multipliers λ and ν we seek a minimum of the function that also involves the Fisher information:

$$L = \int dx [p'(x)]^2 / p(x) + \lambda \left[\int dx (mx^2/2) p(x) - kT/2 \right] + \nu \left[\int dx p(x) - 1 \right] = \min. \quad (8.3.28)$$

The corresponding Euler Lagrange functional is given by

$$L = p'^2/p + \lambda m x^2 p/2 + \nu p. \quad (8.3.29)$$

On inserting this relation into the Euler-Lagrange equation we obtain

$$2 \frac{d}{dx} \left[\frac{p'}{p} \right] + \left[\frac{p'}{p} \right]^2 - \frac{1}{2} \lambda m x^2 - \nu = 0. \quad (8.3.30)$$

For convenience we define an auxiliary function

$$h(x) \equiv \frac{p'(x)}{p(x)} \quad (8.3.31)$$

that converts Eq. (8.3.30) to the Riccati equation

$$2h'(x) + h^2(x) - \frac{1}{2}\lambda mx^2 - \nu = 0. \quad (8.3.32)$$

As may be verified by direct substitution, one solution of this equation is given by $h(x) = Bx$, where, B is an arbitrary constant. One may then solve the above equation for x . However, for present purposes it suffices to replace $h(x)$ in Eq. (8.3.31) by Bx and to solve the resulting differential Eq. (8.3.31) for $p(x)$ to obtain

$$p(x) = a \exp(-b^2 x^2) \quad (8.3.33)$$

For convenience, the constant in the exponent has been taken as $-b^2$. One may determine the constants a and b^2 by substituting Eq. (8.3.33) into the constraint relations (8.3.26) and (8.3.27). The definite integrals (with limits $-\infty$ to ∞) converge to $\sqrt{\pi}/b$ and to $\sqrt{\pi}/2b^3$, respectively. One thus obtains

$$p(x) = \left[\frac{m}{2\pi kT} \right]^{1/2} \exp\left(\frac{-mx^2}{2kT}\right), \quad (8.3.34)$$

which is the *Maxwell Boltzmann distribution law* for one dimension.

You are referred to Ref. 3 for a variety of other, well-known laws, all of which are seen to be based on one fundamental principle, which is a remarkable unification.

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Reprise to the Second Law. Mathematical Proof of the Carathéodory Theorem and Resulting Interpretations

9

9.1 Fundamentals

In Chapter 1, we had introduced functions of state that are mathematical analytic functions of the general form

$$R = R(x_1, \dots, x_i, \dots, x_n), \quad (9.1.1)$$

in which the function R is uniquely specified by the values of the n independent variables x_i for the thermodynamic properties of the system. The corresponding linear differential form is given by

$$dR = \sum_{i=1}^n (\partial R / \partial x_i)_{x_{j \neq i}} dx_i, \quad (9.1.2)$$

and in Chapter 1 was labeled an *exact differential*.

In thermodynamic studies, we have frequent occasion to examine linear differentials of the form

$$\delta L = \sum_{i=1}^n X_i(x_1, \dots, x_i, \dots, x_n) dx_i \quad (9.1.3)$$

that resemble Eq. (9.1.2); these are called *Pfaffian forms*. Here δL is simply a short-hand notation for the function on the right, whose values depend on the selected path, in the sense that the X_i can no longer be determined by differentiation of the single function R in the manner shown in Eq. (9.1.2). The X_i are no longer partial derivatives of a function of state. The entities L occur very frequently in the description of thermodynamic processes but should be replaced, wherever possible, by functions of state, so as to avoid the necessity of having to deal with path-dependent quantities.

Integrable Functions

If a function L does not admit of an exact differential of the form (9.1.2), it may nevertheless be possible, under conditions established below, to introduce functions q such that the ratio $\delta L/q = dR$ does constitute an exact differential. Pfaffian forms of this genre are of special interest; they are said to

be *holonomic* or *integrable*. For obvious reasons, q is said to be an *integrating denominator* and $1/q$, an *integrating factor*.

The particular equation

$$\mathfrak{d}L = \sum_{i=1}^n X_i(x_1, \dots, x_i, \dots, x_n) dx_i \equiv \mathbf{X} \cdot d\mathbf{x} = 0 \quad (9.1.4)$$

is of special interest. If it happens to represent an exact differential, then Eq. (9.1.2) applies $\mathfrak{d}L = dR$, and an *algebraic equivalent* exists, that has the form

$$R(x_1, \dots, x_i, \dots, x_n) = C, \quad (9.1.5)$$

where C is a constant. Equation (9.1.5) specifies an interrelation between the independent variables x_i . In the n -dimensional hyperspace that is spanned by these particular variables, the particular function $R(x_1, \dots, x_i, \dots, x_n) = C$ is representable as a hypersurface of $n - 1$ dimensions in that space. As discussed below, the special relation (9.1.4) represents the curve on that surface.

If $\sum_i X_i dx_i$ is not an exact differential but is nevertheless holonomic, then it has an associated integrating factor such that $q dR = \sum_i X_i dx_i$, whence

$$X_i(x_1, \dots, x_n) = q(\partial R / \partial x_i)_{x_j \neq i}. \quad (9.1.6)$$

Furthermore, Eq. (9.1.4) then implies that $(1/q) \sum_i X_i dx_i = 0$; hence, $dR = 0$, which establishes the existence of an algebraic equivalent, Eq. (9.1.5), to Eq. (9.1.4). If the Pfaffian form is holonomic, then the X_i that are functions of $(\partial R / \partial x_i)_{x_j \neq i}$ by Eq. (9.1.6) may be thought of as components of a vector \mathbf{X} which is proportional to the gradient ∇R of the function R , as indicated on the right of Eq. (9.1.6). Similarly, the various dx_i may be thought of as components of a displacement vector $d\mathbf{x} = \{dx_i\}$.

By its very definition, the gradient of R is everywhere orthogonal to the surface S specified by $R = C$. Therefore, \mathbf{X} (with components $X_i = (\partial R / \partial x_i)$) likewise points in the direction normal to the surface S . Moreover, the requirement $\mathbf{X} \cdot d\mathbf{x} = 0$ is met by requiring $d\mathbf{x}$ to be perpendicular to \mathbf{X} , that is, tangent at all points to the surface S . Therefore, the *solution curves* C formed by adjoining all the $d\mathbf{x}$ segments must lie entirely on the surface S defined by Eq. (9.1.5). It should be self-evident that there exists a throng of points in the hyperspace, outside the surface S , that are not accessible via the solution curves C .

Carathéodory's Theorem

We have so far demonstrated that if Eq. (9.1.3) is holonomic and if Eq. (9.1.4) applies, these conditions are sufficient to guarantee that in any neighborhood of a given point \mathbf{x}_0 in the hyperspace, there exist other points corresponding to Eq. (9.1.5) that are not accessible from \mathbf{x}_0 via solution curves that are subject to the relation $\mathbf{X} \cdot d\mathbf{x} = 0$.

Is the converse also true? That is to say, from the assumption of nonaccessibility can one deduce that $\sum_i X_i dx_i$ is holonomic? The answer is in the affirmative and is furnished through Carathéodory's theorem:

If every neighborhood of an arbitrary point \mathbf{x}_0 in a hyperspace contains points not accessible from it via solution curves of the equation $\sum_i X_i dx_i = 0$, then the Pfaffian form $\mathfrak{d}L = \sum_i X_i dx_i$ is holonomic.

The proof of this important theorem is provided in the next two sections.

9.2 Proof of Holonomicity

We digress here to specify necessary and sufficient conditions to establish whether or not the Pfaffian form $\mathfrak{d}L = \sum_i X_i dx_i$ is holonomic.

Integrability of Linear Forms of Two Variables

We first prove that any linear form involving two variables is integrable: given

$$\mathfrak{d}L = X_1 dx_1 + X_2 dx_2, \quad (9.2.1)$$

we seek a function $q(x_1, x_2)$ such that this form obeys the relation

$$\mathfrak{d}L = qdR, \quad (9.2.2)$$

where dR is an exact differential of the form

$$dR = (\partial R / \partial x_1) dx_1 + (\partial R / \partial x_2) dx_2. \quad (9.2.3)$$

Because of Eqs. (9.2.1–9.2.3) we require that

$$X_1 dx_1 + X_2 dx_2 = q(\partial R / \partial x_1) dx_1 + q(\partial R / \partial x_2) dx_2, \quad (9.2.4)$$

which for arbitrary dx_1 and dx_2 means that

$$X_1 = q(\partial R / \partial x_1) \quad \text{and} \quad X_2 = q(\partial R / \partial x_2). \quad (9.2.5)$$

In principle, these last two relations can always be solved for q and R , since X_1 and X_2 are the established functions of the x_i . We can then construct the ratio

$$\frac{X_1}{X_2} = \frac{(\partial R / \partial x_1)_{x_2}}{(\partial R / \partial x_2)_{x_1}} = - \left[\frac{\partial x_2}{\partial x_1} \right]_R. \quad (9.2.6)$$

One should note how the displacement vector components are related through the X_i .

We conclude that the Pfaffian form (9.2.1) is always integrable since Eq. (9.2.5) represents a set of simultaneous relations that may be solved for q and R . However, this scheme fails if a function of three or more variables, such as $\mathfrak{d}L = X_1 dx_1 + X_2 dx_2 + X_3 dx_3$, was to be examined. One would then have to adjoin to Eq. (9.2.5) the additional relation $X_3 = q(\partial R / \partial x_3)$. It is no longer clear whether this is possible; in fact, we now address precisely this question.

Integrability of Linear Forms of Many Variables

In the more general case, one seeks a function $q(x_1, \dots, x_n)$ such that $(1/q)\mathfrak{d}L = dR$, where $R(x_1, \dots, x_n)$ is a function that (in contrast to $\mathfrak{d}L$) has an associated differential form

$$dR = \sum_{i=1}^n (\partial R / \partial x_i) dx_i \equiv \sum_{i=1}^n Y_i dx_i. \quad (9.2.7)$$

We now examine the necessary conditions for this scheme to work. If indeed a function q_i with the desired properties has been found, then comparison of $\mathfrak{d}L = qdR$ with Eq. (9.2.7) shows that

$$X_i = qY_i = q(\partial R / \partial x_i) \quad (9.2.8)$$

must hold. For the special case $n = 3$, one then finds

$$(\partial R/\partial x_1) \equiv Y_1 = X_1/q, \quad (\partial R/\partial x_2) \equiv Y_2 = X_2/q, \quad (\partial R/\partial x_3) \equiv Y_3 = X_3/q. \quad (9.2.9)$$

Since the order of differentiation is immaterial, we may find a relation between any of the two functions listed in Eq. (9.2.9) according to the following procedure:

$$\frac{\partial^2 R}{\partial x_2 \partial x_1} = \frac{\partial Y_1}{\partial x_2} = \frac{1}{q} \frac{\partial X_1}{\partial x_2} - \frac{X_1}{q^2} \frac{\partial q}{\partial x_2} = \frac{\partial^2 R}{\partial x_1 \partial x_2} = \frac{\partial Y_2}{\partial x_1} = \frac{1}{q} \frac{\partial X_2}{\partial x_1} - \frac{X_2}{q^2} \frac{\partial q}{\partial x_1}. \quad (9.2.10)$$

The central and last terms of the above sequence may be combined to obtain

$$q \left[\frac{\partial X_1}{\partial x_2} - \frac{\partial X_2}{\partial x_1} \right] = X_1 \frac{\partial q}{\partial x_2} - X_2 \frac{\partial q}{\partial x_1}. \quad (9.2.11a)$$

Using similar procedures for the remaining partial derivatives of R , one obtains

$$q \left[\frac{\partial X_3}{\partial x_1} - \frac{\partial X_1}{\partial x_3} \right] = X_3 \frac{\partial q}{\partial x_1} - X_1 \frac{\partial q}{\partial x_3} \quad (9.2.11b)$$

$$q \left[\frac{\partial X_2}{\partial x_3} - \frac{\partial X_3}{\partial x_2} \right] = X_2 \frac{\partial q}{\partial x_3} - X_3 \frac{\partial q}{\partial x_2}. \quad (9.2.11c)$$

Next, multiply Eqs. (9.2.11a,b,c) by X_3 , X_2 , X_1 , respectively, and add the resultants. The sum is found to vanish identically, whence the common factor q may be dropped. This leaves

$$X_1 \left[\frac{\partial X_2}{\partial x_3} - \frac{\partial X_3}{\partial x_2} \right] + X_2 \left[\frac{\partial X_3}{\partial x_1} - \frac{\partial X_1}{\partial x_3} \right] + X_3 \left[\frac{\partial X_1}{\partial x_2} - \frac{\partial X_2}{\partial x_1} \right] = 0. \quad (9.2.12)$$

We see then that if an integrating factor $1/q$ exists that converts the Pfaffian dL into the exact differential Eq. (9.2.7), then the coefficients in the relation $dL = X_1 dx_1 + X_2 dx_2 + X_3 dx_3$ are subject to the requirement (9.2.12). For the more general case of $n > 3$, we obtain very similar relations, with 1, 2, and 3 in Eq. (9.2.12) being replaced by indices i , j , and k that are cyclically permuted, in the manner shown in Eq. (9.2.20) below.

Next, we seek the inverse: given a Pfaffian form

$$dL = \sum_{i=1}^n X_i dx_i, \quad (9.2.13)$$

in which the X_i are subject to the requirement (9.2.12), with cyclic indices i , j , and k , we now establish that there will always exist an integrating factor $1/q$ that converts the inexact differential into an exact differential of the type displayed in Eq. (9.2.7). To prove this, turn to Eq. (9.2.13) and hold the quantities x_n, \dots, x_{n-2} fixed. Equation (9.2.13) then reduces to the form $X_{n-1} dx_{n-1} + X_n dx_n$, which is certainly integrable. Thus, one must be able to find a function H with a differential form analogous to Eq. (9.2.3), as well as an integrating denominator ω such that

$$X_{n-1} dx_{n-1} + X_n dx_n = \omega dH \quad (9.2.14)$$

Since X_{n-1} and X_n are both functions of all x_i , ω and H will likewise depend on these variables. Now relax the constancy requirement and write

$$dH = \sum_{i=1}^n (\partial H / \partial x_i) dx_i. \quad (9.2.15)$$

In order to match up Eq. (9.2.15) with its more restrictive counterpart Eq. (9.2.14), we rewrite the above equation in the form

$$X_{n-1} dx_{n-1} + X_n dx_n = \omega \left[dH - \sum_{i=1}^{n-2} (\partial H / \partial x_i) dx_i \right]. \quad (9.2.16)$$

At this point, reformulate the Pfaffian as

$$\sum_{i=1}^{n-2} X_i dx_i + X_{n-1} dx_{n-1} + X_n dx_n = \mathfrak{d}L \quad (9.2.17)$$

and substitute from Eq. (9.2.16). Also set $\mathfrak{d}L = 0$. Then

$$\sum_{i=1}^{n-2} [X_i / \omega - (\partial H / \partial x_i)] dx_i + dH = \mathfrak{d}L / \omega = 0. \quad (9.2.18)$$

At this stage, let us switch variables: we set $y_i \equiv x_i$ for $i = 1, 2, \dots, n-2, n$ and set $y_{n-1} = H(x_1, \dots, x_n)$. This renders y_{n-1} a function of all independent variables. Last, set $Y_i \equiv X_i / \omega - (\partial H / \partial x_i)$ for $i = 1, 2, \dots, n-2$. Then Eq. (9.2.18) takes the form

$$\sum_{i=1}^{n-2} Y_i dy_i + dy_{n-1} = \mathfrak{d}L / \omega = 0. \quad (9.2.19)$$

This expression contains one fewer variable than the corresponding form (9.2.17). Unfortunately, the Y_i would seem to depend on all the variables y_1, y_2, \dots, y_n . To show that this is not the case, we proceed as follows: since we passed from Eqs. (9.2.17)–(9.2.19) by purely algebraic transformations, the former equation will be integrable if the latter is. By hypothesis, Eq. (9.2.12) applies to Eq. (9.2.17); hence, a corresponding relation will have to hold for Eq. (9.2.19), namely

$$Y_i \left[\frac{\partial Y_j}{\partial y_k} - \frac{\partial Y_k}{\partial y_j} \right] + Y_j \left[\frac{\partial Y_k}{\partial y_i} - \frac{\partial Y_i}{\partial y_k} \right] + Y_k \left[\frac{\partial Y_i}{\partial y_j} - \frac{\partial Y_j}{\partial y_i} \right] = 0. \quad (9.2.20)$$

Apply the above relation to the special case $j = n-1, k = n$. But, according to Eq. (9.2.19), $y_{n-1} = 1$ and $y_n = 0$. Hence Eq. (9.2.20) reduces to

$$(\partial Y_i / \partial y_n) = 0 \quad \text{for all } i. \quad (9.2.21)$$

This demonstrates that in fact none of the Y_i in Eq. (9.2.19) depends on y_n . Thus, Eq. (9.2.19) involves only the $n-1$ independent variables y_1, \dots, y_{n-1} .

We now repeat the entire process, beginning with Eq. (9.2.14), and ending with Eq. (9.2.19), which contains one fewer variable than its equivalent, Eq. (9.2.17). In the final iteration, the analog of Eq. (9.2.19) contains only two variables and thus is integrable, so long as Eq. (9.2.20) continues to hold.

9.3 Necessary Condition for Establishing the Carathéodory's Theorem

In Section 9.1, we had established sufficiency requirements that relate to Carathéodory's theorem. We now attend to formulate the necessary statement by proving the following:

If in every neighborhood of any point in the space spanned by the set $\{x_i\}$, $i = 1, \dots, n$, there are points inaccessible along solution curves $\sum_i X_i dx_i = 0$, then the corresponding Pfaffian form $dL = \sum_i X_i dx_i$ is necessarily integrable.

As is well established, a curve C in a hyperspace may be defined as a collection of all points generated by equations of the form

$$x_i = f_i(u) \quad (i = 1, 2, \dots, n), \quad (9.3.1)$$

where the f_i represent continuous, differentiable, single-valued functions involving a relevant parameter u , which frequently is simply time. Let points P_a and P_b correspond to two specific choices for u , with $u_a < u < u_b$. Let C_a be another curve that intersects C at u_a and that otherwise differs from C only infinitesimally. Then C_a is specified by an equation of the form

$$x_i = f_i(u) + \varepsilon \varphi_i(u) \quad (i = 1, 2, \dots, n) \quad (9.3.2)$$

in which ε is a small quantity, and $\varphi_i(u)$ is another function analogous to $f_i(u)$, with the constraint that

$$\varphi_i(u_a) = 0 \quad (\text{all } i). \quad (9.3.3)$$

Moreover, since C and C_a are the solution curves, they are subjected to the requirement (9.3.4); that is, we set

$$\sum_{i=1}^n X_i(x_i) f'_i(u) = 0, \quad (9.3.4)$$

where the prime indicates the partial derivative with respect to u . In what follows we also will set $Y_i(u) \equiv X_i(f_i(u))$ whenever we wish to emphasize the dependence of X_i on u . The same requirement must be met by the displaced curve:

$$\sum_{i=1}^n X_i[f_i(u) + \varepsilon \varphi_i(u)] \cdot [f'_i(u) + \varepsilon \varphi'_i(u)] = 0. \quad (9.3.5)$$

We expand the argument of X_i in a Taylor's series to first order in ε . This yields

$$\sum_{i=1}^n Y_i(u) (f'_i(u) + \varepsilon \varphi'_i(u)) + \sum_{i=1}^n \sum_{j=1}^n \varepsilon \varphi_j(u) \left(\frac{\partial X_i}{\partial x_j} \right) f'_i(u) = 0. \quad (9.3.6)$$

On account of Eq. (9.3.4), the above simplifies to

$$\sum_{i=1}^n X_i \varphi'_i + \sum_{i=1}^n \sum_{j=1}^n (\partial X_i / \partial x_j) \varphi_j f'_i = 0. \quad (9.3.7)$$

This expression may be satisfied by arbitrarily selecting $n - 1$ functions and requiring the remaining one, say, φ_k , to conform to the condition set by Eq. (9.3.7). To do this, rewrite Eq. (9.3.7) in the following form:

$$X_k \varphi'_k + \sum_{i=1}^n \left(\frac{\partial X_i}{\partial x_k} \right) f'_i \varphi_k = - \sum_{j=1}^{n-1} X_j \varphi'_j - \sum_{i=1}^n \sum_{j=1}^{n-1} \left(\frac{\partial X_i}{\partial x_j} \right) f'_i \varphi_j. \quad (9.3.8)$$

The prime symbol on the summation sign indicates that the term $i = k$ or $j = k$ is to be omitted from the summation. This first-order differential Eq. (9.3.8) is ultimately solved for φ_k by the standard technique of finding a multiplier $\lambda(u)$ for both sides of Eq. (9.3.8) that converts the left into a differential function of the form

$$\frac{d(\lambda X_k \varphi_k)}{du} \equiv \lambda X_k \varphi'_k + \lambda \sum_{i=1}^n \left(\frac{\partial X_k}{\partial x_i} \right) f'_i \varphi_k + \lambda' X_k \varphi_k, \quad (9.3.9)$$

where Eq. (9.3.2) was invoked, while retaining only terms to the first order. Comparison with Eq. (9.3.8), multiplied by λ , shows that if an identity is to be reached, then the function λ must satisfy the relation

$$\lambda' = (\lambda/X_k) \sum_{i=1}^n \left(\frac{\partial X_i}{\partial x_k} - \frac{\partial X_k}{\partial x_i} \right) f'_i. \quad (9.3.10)$$

Next, multiply both sides of Eq. (9.3.8) by λ and introduce Eq. (9.3.9) to eliminate $X_k \varphi'_k$. Then eliminate λ' in the intermediate step by using Eq. (9.3.10). Integration of the resultant and subsequent use of Eq. (9.3.3) leads to

$$\lambda X_k \varphi_k = - \int_{u_a}^u \lambda \left[\sum_{j=1}^{n-1} X_j \varphi'_j + \sum_{i=1}^n \sum_{j=1}^{n-1} \left(\frac{\partial X_i}{\partial x_j} \right) f'_i \varphi_j \right] du. \quad (9.3.11)$$

We treat the first integral on the right by integration by parts:

$$- \int_{u_a}^u \lambda \sum_{j=1}^{n-1} X_j \varphi'_j du = - \lambda \sum_{j=1}^{n-1} X_j \varphi_j + \int_{u_a}^u \lambda' \sum_{j=1}^{n-1} X_j \varphi_j du + \int_{u_a}^u \lambda \sum_{j=1}^{n-1} \sum_{i=1}^n \left(\frac{\partial X_j}{\partial x_i} \right) f'_i \varphi_j du, \quad (9.3.12)$$

where Eq. (9.3.3) was again used to obtain the first term on the right, and Eq. (9.3.1) was introduced to write out the last term.

At this point, eliminate λ' by use of Eq. (9.3.10); this yields

$$- \int_{u_a}^u \lambda \sum_{j=1}^{n-1} X_j \varphi'_j du = - \lambda \sum_{j=1}^{n-1} X_j \varphi_j + \int_{u_a}^u \lambda \sum_{i=1}^n \sum_{j=1}^{n-1} (f'_i \varphi_j) \times \left[\left(\frac{\partial X_i}{\partial x_k} - \frac{\partial X_k}{\partial x_i} \right) \frac{X_j}{X_k} + \frac{\partial X_j}{\partial x_i} \right] du. \quad (9.3.13)$$

This resultant may now be substituted in Eq. (9.3.11); on simplifying, one obtains

$$\varphi_k = - \sum_{j=1}^{n-1} \frac{X_j}{X_k} \varphi_j - \frac{1}{\lambda X_k} \sum_{i=1}^n \sum_{j=1}^{n-1} \int_{u_a}^u \lambda \left(\frac{f'_i \varphi_j}{X_k} \right) \times \left[X_j \left(\frac{\partial X_k}{\partial x_i} - \frac{\partial X_i}{\partial x_k} \right) + X_k \left(\frac{\partial X_i}{\partial x_j} - \frac{\partial X_j}{\partial x_i} \right) \right] du. \quad (9.3.14)$$

Finally, observe that on account of Eq. (9.3.4), one may add the term

$$-\frac{1}{\lambda X_k} \int_{u_a}^u \sum_{i=1}^n {}' \sum_{j=1}^{n-1} \frac{f'_i \phi_j}{X_k} \lambda X_i \left(\frac{\partial X_j}{\partial x_k} - \frac{\partial X_k}{\partial x_j} \right) du = 0 \quad (9.3.15)$$

without changing Eq. (9.3.15) since solely the summand $f'_i \phi_j$ is involved in the summation over i and this sum vanishes. When Eq. (9.3.15) is adjoined to Eq. (9.3.14), one finally obtains

$$\phi_k(u) = -\sum_{j=1}^{n-1} \frac{X_j}{X_k} \phi_j(u) - \frac{1}{\lambda X_k} \sum_{i=1}^n {}' \sum_{j=1}^{n-1} {}' \int_{u_a}^u \lambda \left(\frac{f'_i \phi_j(u)}{X_k} \right) F_{ijk} du, \quad (9.3.16)$$

in which F_{ijk} is defined by the left-hand side of Eq. (9.2.20), with the interchanges $Y \leftrightarrow X$ and $y \leftrightarrow x$. Now examine Eq. (9.3.16) after replacing the upper limit on the integral by u_b . Observe that $\phi_k(u_b)$ on the left depends not only on all $\phi_j(u_b)$ in the first term on the right but also on the values that these $\phi_j(u)$ take over the entire interval $u_a \leq u \leq u_b$ when the integration in the second term is carried out. Hence, one may choose the *arbitrary* functions $\phi_j(u)$ in such a manner that from point P_a , one may reach any other point in its neighborhood. For example, one may select u_b sufficiently close to u_a and permute the indices so that all n functions ϕ_j are successively assigned the index k . However, this is contrary to the initial hypothesis; we assumed at the outset that in the neighborhood of P_a , there were points inaccessible from P_a . The only way to avoid this impasse is to demand that all integrals in Eq. (9.3.16) vanish. We cannot allow λ , ϕ_j , or $1/X_k$ to be equal to zero, for then all else would be lost. The only viable option is to require that

$$\sum_{i=1}^n {}' F_{ijk} f'_i = 0; \quad (9.3.17)$$

for, in that event, the integral drops out and $\phi_n(u_b)$ then depends only on the specific values that the $n - 1$ arbitrary functions ϕ_j assume at the location $u = u_b$. This clearly limits the number of curves that can be constructed to pass through P_a , and hence restricts the number of points P_b that can be reached from P_a .

According to Eq. (9.3.17), we then require either that all f'_i be zero or that all F_{ijk} vanish. The first alternative cannot be correct since all the functions f_i except f_k may be chosen arbitrarily and f_k is absent from the summation over i . This leaves only the alternative that all $F_{ijk} = 0$. From the earlier discussion involving Eq. (9.2.20), it follows that the Pfaffian $dL = \sum_i X_i dx_i$ is integrable. We have thereby established the necessary condition for the Carathéodory's theorem of Section 9.2 to hold. Given the fact that in the neighborhood of a point in phase space other points are inaccessible via solution curves of the form $\sum_i X_i dx_i = 0$, the Pfaffian form is integrable.

9.4 Relevance to Thermodynamics

We now utilize the machinery of the preceding sections to rationalize the Second Law of Thermodynamics as specified by Carathéodory:

In the neighborhood of any state of an adiabatically isolated system there exist states that are inaccessible from that state.

According to the previous line of argument, this implies that when the condition $dQ = 0$ is met, there exist inaccessible states such that the linear form $\delta_r Q = \sum_i X_i dx_i$ may be converted into the differential of a function of state, the metrical entropy, ds , through an integrating factor λ , by which $ds = \delta_r Q / \lambda$. By the reasoning of Section 1.8, this relation may be converted to the standard form $dS = \delta_r Q / T$ that is then directly linked to the Second Law. Once the above postulate is accepted, this function of state is directly derived from a mathematical construct, rather than resting solely on an empirical foundation, as set forth in Section 1.8. To individuals favoring a mathematical development of the subject matter, instead of an assertion resting on purely experimental investigations, this may be a preferred alternative.

By use of the Carathéodory approach, one may also draw a parallel between the First and Second laws. Briefly repeating the remarks of the last paragraph, we adapt the above postulate to the performance of work. We note that from the absence of any infinitesimal heat exchange for the linear form $\delta_r Q = \sum_i X_i dx_i = 0$ in an adiabatic system, one may infer the existence of a function of state s (hence, the function of state S) that is a constant under this condition. In a similar manner, one may apply Carathéodory's theorem to the existence of the linear form $\delta_r W = \sum_i Z_i dz_j$ for performance of work. On specializing to an adiabatic system and then imposing the requirement $dW = 0$, the same theorem *necessitates* the existence of another function of state, called the *internal energy* E , which is a constant. This provides another perspective on the introduction of the First Law, with obvious implications concerning the conservation of energy. Such a development may again appeal to those who wish to emphasize the mathematical development of the subject matter.

Beyond this point, one must be aware of important differences between the two laws. The performance of work is directly linked to changes in energy of a system, so that the integrating factor q relevant to the First Law is unity. Furthermore, changes in S are tracked by the *reversible* transfer of heat across the boundaries of the system or by other reversible changes of state. Additional changes in S are incurred when irreversible processes occur; this subject was treated in detail in Section 1.10. By contrast, alterations in E are tracked by performance of work, whether reversibly or irreversibly, under adiabatic conditions. Different changes in E are incurred when these processes take place under nonadiabatic conditions, as discussed in Section 1.7.

9.5 Derivation of the Limiting Form for the Debye–Hückel Equation

Fundamentals

In this introductory foray into the subject, we present a simplified derivation of the Debye–Hückel equation, guided by the exposition of Ref. 1, which is also of intrinsic interest. References to a more complete exposition are listed in Ref. 2.

Consider a collection of positive and negative ions in a solution in appropriate concentrations so as to preserve electroneutrality. Single out a particular cation³, termed the *central ion*, located within the volume element dr^3 surrounding the position \mathbf{r}_1 . The electrostatic potential ψ that is generated by all the other charges in the solution is (generally) spherically symmetric: at a given position \mathbf{r}_2 away from \mathbf{r}_1 , ψ has the same value at any point on the surface of a sphere of radius $r = |\mathbf{r}_2 - \mathbf{r}_1|$ centered on \mathbf{r}_1 . As the central ion moves through the solution, the sphere moves with it; hence, we may dispense with the angular coordinates; the electrostatic interactions depend solely on the separation distance between ions. These interactions produce a nonuniform, time-averaged distribution of the ionic

constellation: the coions and counterions on average are, respectively, spaced further apart from and closer to the central cation as compared to the average separation that prevails in the absence of interactions. The Debye–Hückel theory specifies deviations from thermodynamic ideality that are generated by the electrostatic interactions.

As shown in Sections 1.5 and 1.6, the electrostatic work involved in moving an element of charge dq from infinity to a location characterized by the electrostatic potential ψ is $\delta w = \psi dq = \pm z_i e \psi dn$, where z_i is the ionic valence; $-e$ and $+e$ are the electronic charges on negatively and positively charged ions, respectively. The chemical potential for a given central ion of type i at location r is thus specified as

$$\mu_i(\mathbf{r}) = \mu_i^* + k_B T \ln c_i(\mathbf{r}) \pm z_i e \psi(\mathbf{r}), \quad (z_i > 0). \quad (9.5.1)$$

The electrostatic potential ψ acting on ion i , and its concentration c_i is determined by the disposition of all other electric charges, and varies with \mathbf{r} . Until later we drop the subscript i and note that at equilibrium, as a necessary condition, the chemical potential of a test ion must be the same at two different locations \mathbf{r}_1 and \mathbf{r}_2 . On imposing this condition on a positive test charge, we rearrange Eq. (9.5.1) to read

$$\ln \frac{c(r_2)}{c(r_1)} = -ze \frac{\psi(r_2) - \psi(r_1)}{k_B T}, \quad (9.5.2)$$

where we dropped the vectorial notation. Now consider the interaction of the central ion with another one of its kind, and move this second ion to infinity where $\psi(r_1) = 0$, and where $c(r_1) = c$, which is the normal concentration of the species in the absence of all ionic interactions. We then find that for positively charged ions,

$$c_+(r) = c_+ \exp[-ze\psi(r)/k_B T], \quad (9.5.3a)$$

while for negatively charged counterions,

$$c_-(r) = c_- \exp[+ze\psi(r)/k_B T]. \quad (9.5.3b)$$

The charge density from the two types of ions at location r is given by

$$\rho(r) = e[z_+ c_+(r) - z_- c_-(r)]. \quad (9.5.3c)$$

We suppress the r dependence, and note that Eq. (9.5.3c) is to be interpreted as a local rather than as a global relation. For more than one set of coions and counterions in solution, a summation must be carried out, whereby Eq. (9.5.3c) is generalized to

$$\rho(r) = e \sum_i (z_{i+} c_{i+} - z_{i-} c_{i-}), \quad (9.5.3d)$$

where i enumerates the distinct chemical species from which the ions are derived.

We next introduce Gauss' law in the form $\nabla \cdot \mathcal{E} = \rho/\epsilon_0 \epsilon$, where \mathcal{E} is (to a good approximation) the dielectric constant of the solvent, ϵ_0 is the permittivity of the vacuum, and ϵ is the prevailing electrostatic field. On setting $\mathcal{E} = -\nabla\psi$, we find that

$$\nabla^2 \psi = -\rho/\epsilon_0 \epsilon, \quad (9.5.4)$$

which is *Poisson's equation*. After introducing Eqs. (9.5.3a,b,d), one obtains

$$\nabla^2\psi = -(e/\epsilon_0\epsilon)\sum_i [z_{i+}c_{i+} \exp(-z_{i+}e\psi/k_BT) - z_{i-}c_{i-} \exp(+z_{i-}e\psi/k_BT)], \quad (9.5.5a)$$

which is a transcendental equation that in its full form can only be handled numerically. To continue the analytic treatment, we note that ordinarily the potentials arising from the negative and positive ionic charges nearly cancel out. This allows us to introduce the first-order expansion of the exponential functions, so that, for $ze\psi \ll k_BT$,

$$\begin{aligned} \nabla^2\psi &= -(e/\epsilon_0\epsilon)\sum_i [z_{i+}c_{i+}(1 - z_{i+}e\psi/k_BT) - z_{i-}c_{i-}(1 + z_{i-}e\psi/k_BT)] \\ &= (e^2\psi/k_BT\epsilon\epsilon_0)\sum_i (z_{i+}^2c_{i+} + z_{i-}^2c_{i-}) \equiv 2e^2\psi S/k_BT\epsilon\epsilon_0. \end{aligned} \quad (9.5.5b)$$

Here, we imposed the electroneutrality constraint, whereby the summation $\sum_i z_i c_i$ vanishes. We also introduced the concept⁴ of *ionic strength*, introduced in Eq. (4.2.1) as $S = 1/2\sum_i z_i^2 c_i$.

The above relation may be recast as

$$\nabla^2\psi = -k^2\psi = (1/r)[d^2(r\psi)/dr^2], \quad (9.5.5c)$$

$$k^2 \equiv e^2\sum_i (z_{i+}^2c_{i+} + z_{i-}^2c_{i-})/\epsilon_0\epsilon k_BT = 2e^2S/\epsilon_0\epsilon k_BT, \quad (9.5.5d)$$

where the right-hand side of Eq. (9.5.5c) represents the second derivative for spherically symmetric coordinates. We thus need to solve the differential equation

$$\frac{d^2(r\psi)}{dr^2} = \kappa^2(r\psi), \quad (9.5.5e)$$

whose solution (as may be verified by direct substitution) for the potential of the central ion is given by

$$\psi(r) = \frac{C_1}{r}e^{\kappa r} + \frac{C_2}{r}e^{-\kappa r}, \quad (9.5.6)$$

where C_1 and C_2 are the two constants. Their determination requires two boundary conditions. First, we require that the electrostatic potential at an infinite distance $r = \infty$ from the central ion vanish. Since $\exp(\kappa r)/r$ increases indefinitely with r , we must set $C_1 = 0$. The second condition hinges on adopting a model of the central ion as a sphere of radius a . At that particular distance from its center, its potential has the value

$$\psi(a) = \frac{C_2}{a}e^{-\kappa a}, \quad (9.5.7)$$

whose substitution in Eq. (9.5.6) leads to

$$\psi(r) = \frac{a\psi(a)}{r}e^{-\kappa(r-a)}, \quad (r \geq a). \quad (9.5.8)$$

The Electrostatic Potential at $r = a$

To determine $\psi(a)$, we note that the electrostatic potential, as a solution to a second-order differential equation, must be continuous and vary smoothly across the boundary at $r = a$ which separates the ion from its surroundings. For further ease of operations, we now represent the ion as a sphere whose entire

charge, Q_e , is uniformly distributed over the inside surface—the balloon model of an ion. This may be justified by appealing to a consequence of Gauss' law: any uniform charge distribution within an enclosed sphere has the same effect on the outside world as if the entire charge was concentrated at its center. As is seen later, the balloon model represents a very convenient special uniform charge distribution within the sphere.

For continuity, we require the first derivative of Eq. (9.5.8), to be evaluated at $r = a$. Standard differentiation leads to

$$\left[\frac{d\psi}{dr} \right]_{r=a} = -\psi(a) \frac{1 + \kappa a}{a}. \quad (9.5.9)$$

We now determine the relevant potential in two different ways. For locations outside the sphere, the electric field is given by $E = Q_e / 4\pi\epsilon\epsilon_0 r^2$, where r is the distance from the center and Q_e , the charge on the balloon; then, the corresponding potential is found by integration

$$\psi_o(r) = - \int_{\infty}^r \left(\frac{Q}{4\pi\epsilon\epsilon_0 r^2} \right) dr = Q_e / 4\pi\epsilon\epsilon_0 r \quad (r \geq a). \quad (9.5.10a)$$

On the other hand, in the interior of the balloon, the electrostatic field vanishes by Gauss' law since no charge is enclosed. (Hence, the clever adoption of the balloon model!,) then $\epsilon = 0$ for $r < a$, whence

$$\psi_i = C_3, \text{ a constant for } r < a. \quad (9.5.10b)$$

Since ψ must match at the boundary, we equate Eq. (9.5.10a) with Eq. (9.5.10b) to find $C_3 = \psi_i(a) = Q_e / 4\pi\epsilon\epsilon_0 a$. Second, at the boundary,

$$\left[\frac{d\psi}{dr} \right]_{r=a} = -\frac{Q_e}{4\pi\epsilon\epsilon_0 a^2}. \quad (9.5.10c)$$

Since the potential must change smoothly across the boundary, this derivative must match the one in Eq. (9.5.9). This enables us to solve for

$$\psi_i(a) = Q_e / 4\pi\epsilon\epsilon_0 a(1 + \kappa a), \quad (9.5.11)$$

which, in turn, may be applied to Eq. (9.5.8) for the final desired relation:

$$\psi(r) = \frac{Q_e}{4\pi\epsilon\epsilon_0 r(1 + \kappa a)} e^{-\kappa(r-a)} \equiv C \frac{Q_e}{\epsilon r(1 + \kappa a)} e^{-\kappa(r-a)} \quad (r \geq a). \quad (9.5.12a)$$

Discussion

The above expression is a fundamental result of importance; it shows how the potential associated with an ion in the presence of others differs from the conventional form $\psi(r) = Q_e / 4\pi\epsilon_0 r$, for an isolated ion in solution, to which it reduces when $\kappa = 0$. As is seen, the potential Eq. (9.5.12a) drops off roughly exponentially with increasing r beyond the radius of the sphere, and the effective charge acting on the outside world is given by $Q_e / (1 + \kappa a)$. This type of decay is characteristic of systems of interacting charges, and is encountered in many other areas in science. One generally refers to this formulation as a *shielded potential*. The degree of reduction of the potential is governed by the magnitude of the exponential decay constant, Eq. (9.5.5d), which thus varies as $\sqrt{(S/\epsilon k_B T)}$. Incidentally, the dielectric

constant ϵ also depends on T . For a particular medium at fixed temperature, the rate of decay thus depends on the square root of the ionic strength. Equation (9.5.12a) also shows that one may consider $1/\kappa$ as representing an average interaction distance: for a 0.1 M solution of ions in water at room temperature, this distance is approximately 10 Å, beyond which the shielding is fully effective.

In many cases of interest, the product κa is small compared to unity, so that Eq. (9.5.12a) reduces to

$$\psi(r) = \frac{CQ_e}{\epsilon r} e^{-\kappa(r-a)} \quad (r \geq a). \quad (9.5.12b)$$

Incidentally—and this is really important—in physical problems where electrons rather than ions act as carriers of negative charge, these fundamental particles are considered to be point charges, with $a = 0$. Then one encounters the commonly quoted result

$$\psi(r) = \frac{CQ_e}{\epsilon r} e^{-\kappa r} \quad (9.5.12c)$$

for the electrostatic potential of electrons in a medium of other electrons, as in a metal.

The origin of the above relations may be traced to the solution to the Poisson equation. When all the ions or electrons are far removed from each other in an infinite copy of the system, κ vanishes; one then obtains the standard expression $\psi = Q_e/4\pi\epsilon\epsilon_0 r$.

Relation to Thermodynamics

To connect the above findings to thermodynamic principles, imagine the hypothetical situation in which all ionic species in the solution are placed in their final positions, but initially are devoid of their charges. We then initiate a reversible charging process that converts each ion from a value $Q_e = 0$ to the value $Q_e = z_i e$. This process may be monitored by introducing a parameter λ that increases from zero to unity during the charging process; λ is thus the fractional charge on the central ion. The required work must be executed reversibly at constant temperature and pressure. Hence, in accord with the discussion in Section 1.12, the charging process involves a change in the Gibbs free energy of the system. Furthermore, this step is precisely the operation responsible for departures from ideality due to the concomitant electrostatic interactions. Therefore, on introducing the relation for the chemical potential of species i per ionic species (rather than per mole),

$$\mu_i = \mu_i^* + k_B T \ln c_i + k_B T \ln \gamma_i, \quad (9.5.13)$$

where γ_i is the activity coefficient for species i , as defined in Section 3.4, we may set

$$k_B T \ln \gamma_i = \int_0^1 z_i e \psi(\lambda) d\lambda. \quad (9.5.14)$$

Here, the differential of work performance is expressed by the integrand; as the charging process proceeds, the electrostatic potential rises as indicated.

The further development hinges on the specification of the potential in Eq. (9.5.14). One contribution involves the work to locate a particular central ion in final form in its aqueous milieu, which quantity is independent of concentration and may therefore be included in the constant term μ_i^* . The second contribution involves the redistribution of ions surrounding the central one, as a result of the charging

process. This requires the specification of an electrostatic potential of the central ion with its coions and counterions relative to its potential in the pure solvent, ψ_0 . We approximate the integration process by recognizing that the maximum value achievable for the potential arises when two ions are in closest proximity, at a distance b , which is the sum of their radii. Hence, we may use Eq. (9.5.11), with a replaced by b , for the corresponding potential. The reference value is that for which the ion resides alone in the pure solvent, whereby $\kappa = 0$ and $Q_e = z_{i+}e$. Thus, for the central cation at a given state of charge λ ,

$$\psi(\lambda) = C \frac{z_{i+}e}{\epsilon} \left[\frac{1}{1 + \kappa b} - 1 \right] \lambda = -C \frac{z_{i+}e}{\epsilon} \frac{\kappa}{1 + \kappa b} \lambda. \quad (9.5.15)$$

Now use Eq. (9.5.14) and execute the integration over λ ; then, for cations of species i ,

$$\ln \gamma_{i+} = -C \mathcal{N} \frac{z_{i+}^2 e^2}{2\epsilon RT} \left[\frac{\kappa}{1 + \kappa b} \right], \quad (9.5.16a)$$

which is the central result of interest. Here \mathcal{N} is Avogadro's number⁵. For the anionic species, we obtain similarly

$$\ln \gamma_{i-} = -C \mathcal{N} \frac{z_{i-}^2 e^2}{2\epsilon RT} \left[\frac{\kappa}{1 + \kappa b} \right]. \quad (9.5.16b)$$

The individual activity coefficients cannot be measured experimentally. They must be combined according to the following scheme: let the dissolved species dissociate as $C_{\nu+}A_{\nu-} \rightarrow \nu_+ C^{z_+} + \nu_- A^{z_-}$, where z_i is regarded as a positive quantity; C and A represent the cations and anions, respectively. The law of electroneutrality demands that $\nu_+ z_+ = \nu_- z_-$. Now define the *valence factor* f as

$$f \equiv (\nu_+ z_+^2 + \nu_- z_-^2) / \nu; \quad \nu \equiv \nu_+ + \nu_-, \quad (9.5.17)$$

and follow convention by introducing the *mean activity coefficient* by the relation

$$\nu \ln \gamma_{\pm} = \nu_+ \ln \gamma_+ + \nu_- \ln \gamma_-. \quad (9.5.18)$$

Using Eqs. (9.5.16), the mean activity coefficient is given by

$$\ln \gamma_{\pm} = -f C \mathcal{N} \frac{z_{i-}^2 e^2}{2\epsilon RT} \left[\frac{\kappa}{1 + \kappa b} \right]. \quad (9.5.19)$$

Equations (9.5.16) and (9.5.19) represent the starting points of the derivations in Section 4.2. The parameter κ is defined via Eq. (9.5.5d), which involves the quantity $\sqrt{(S/\epsilon T)}$. In most cases, the product κb is negligible compared to unity. Then $\ln \gamma_i \propto S^{1/2} (1/\epsilon T)^{3/2}$. Thus, other factors being equal, the logarithm of the activity coefficient for species i (which is governed by all cations and anions in the solution) is predicted to depend principally on the square root of the ionic strength of the solution.

The above is an abbreviated exposition of the fundamental principles. More sophisticated derivations provide better insights on the characteristics of the Debye–Hückel theory. You are encouraged to study these expositions on your own.

References and Query

9.5.1. Ken A. Dill and Sabrina Bromberg, *Molecular Driving Forces, Statistical Thermodynamics in Chemistry and Biology*, (Garland Science, New York, 2003), Chap. 23.

- 9.5.2.** See e.g. A.W. Adamson, *Physical Chemistry of Surfaces*, 3rd Ed. (Wiley, New York, 1976); F.H. MacDougall, *Thermodynamics and Chemistry*, (Wiley, New York, 1939); C.M.A. Brett and A.M.O. Brett, *Principles, Methods, and Applications* (Oxford University Press, New York, 1993).
- 9.5.3.** What changes, if any, would be required if an anion were selected as the central ion?
- 9.5.4.** This is appropriate only to the extent that the difference between molality and molarity can be ignored in aqueous solutions. Why is this the case?
- 9.5.5.** In this and subsequent relations one encounters Avogadro number as a factor in the equations because one uses $\mu = \mu_0 + k_B T \ln a$ as the molecular chemical potential.

10.1 Distributions and Statistics

Here, we provide a superficial review of some of the statistical formulas that have been cited earlier. This certainly is no substitute for an in-depth discussion, for which you need to consult one of the numerous specialized texts on this topic. We follow in part the presentation by (P.A. Rock¹).

For any system of noninteracting particles, quantum mechanics specifies a set of g_i distinct energy levels ε_i , each of which is either unoccupied ($n_i = 0$) or occupied by a variable number n_i of particles; g_i is known as the *degeneracy* of level ε_i . The total number $\sum_i n_i = N$ of particles is fixed. We want to find the total number, Ω , of ways (the distributions) in which the N particles can be assigned to the set of distinct ε_i levels. We then ask for the particular arrangement of particles that corresponds to the most probable value Ω_m , subject to the requirement that the energy $E = \sum_i n_i \varepsilon_i$ of the isolated system remains fixed and subject to further stipulations. There are three cases to consider:

1. *The Boltzmann Distribution*: Distinguishable particles (such as atoms on a lattice) without any restrictions on how many particles can occupy a given energy level ε_i . Such particles will be called *boltzons*.
2. *The Bose–Einstein Distribution*: Indistinguishable particles (such as particles with spin $S = 0$ or $S = 1$ and multiples thereof) without limiting the number that can occupy any state of energy ε_i . Such entities are called *bosons*.
3. *The Fermi–Dirac Distribution*: Indistinguishable particles (such as electrons with spin $S = 1/2$ or multiples thereof) for which the occupancy of any energy level ε_i is restricted to $n_i = 0$ or 1. These entities are termed *fermions*.

Boltzmann Statistics

We construct an analogy by considering a container filled with N identical marbles that are individually numbered and are thereby rendered distinguishable. They are now removed at random one by one and lined up in a row. We ask how many such distinguishable sequences can be generated? The first position can be filled by removing one of the N available marbles; the second position, by removing one of the remaining $N - 1$ marbles; the third position, by selecting one among the

remaining $N - 2$ marbles; and so on, until the last marble has been drawn out. Altogether, we have generated

$$\Omega_i = N \cdot (N - 1) \cdot (N - 2) \cdots 2 \cdot 1 = N! \quad (10.1.1)$$

different distinguishable sequences or *configurations*.

For further visualization, let us place every marble present in a particular sequence Ω_i into a box, and assume temporarily that exactly N boxes are available. We now contemplate the possibility that a given box—the i th—can be filled with more than one marble; let n_i be the number of marbles filling that bin. We have thereby generated some containers that are filled by several marbles, others, containing one marble, and empty boxes as well. Clearly, the length of all the sequences, given by the alignment of only filled boxes, has now been reduced. So has the magnitude of every Ω_i ; for the number of multiplicative factors in the reduced sequence (10.1.1) is now smaller. The question is by how much? Note that a particular sequence Ω_i remains unaltered, no matter in what order the $n_i > 1$ marbles are arranged in the i th receptacle. By the process indicated earlier, we see that there are $n_i!$ ways of filling the i th bin, but all of them are associated with the particular sequence Ω_i . We must therefore divide the original $N!$ states by $n_i!$ so as to count only distinguishable configurations (see footnote 2 for an illustration). This process must be continued to account for all other multiply occupied boxes j, k, l, \dots . Thus, the number of possible configurations is now given by

$$\Omega_{ijkl\dots} = N! / n_i! n_j! n_k! n_l! \cdots \quad (10.1.2)$$

By the same reasoning, all singly occupied boxes contribute $1!$ as a divisor, and all empty boxes, $0! = 1$ as a divisor. Additional $0! = 1$ divisors are included for any boxes that are added to the original N boxes in the lineup.

We next attend to another complication. Suppose each bin, such as the i th, contains g_i subdivisions, or *microstates*, with no restriction on the number of marbles that can be placed in each inner compartment. Then there are g_i choices for the disposition of the first of the n_i marbles in the i th bin; the same choice exists for the second, third, \dots until all n_i have been positioned. Each such choice is termed a *complexion*. The count of distinguishable configurations has thereby been increased by a factor $g_i^{n_i}$ for all occupied boxes, and by the factor $g_i^0 = 1$ for the empty ones. The upshot of all this is that there exist

$$\Omega_B = N! \prod_i \frac{g_i^{n_i}}{n_i!} = N! \cdot \frac{g_1^{n_1}}{n_1!} \cdot \frac{g_2^{n_2}}{n_2!} \cdot \frac{g_3^{n_3}}{n_3!} \cdots \quad (10.1.3)$$

distinct arrangements or configurations that can be generated. The above is termed the *Boltzmann statistical distribution*. It should be obvious how this model applies to a set of distinguishable, non-interacting elementary physical objects that are distributed among distinct energy levels ϵ_i with associated degeneracy g_i . Systems for which g_i greatly exceeds n_i are said to be *dilute*, for which the probability of encountering multiple occupancy of any of the degenerate levels is remote.

Of particular interest is the case where only two different states exist, where $n_1 + n_2 = N$, and $g_1 + g_2 = P$; then $n_1 \equiv n$; $n_2 = N - n$, also, $g_1 \equiv p$ and $g_2 = P - p$, so that

$$\Omega_2 = N! \cdot \frac{p^n}{n!} \cdot \frac{(P - p)^{N - n}}{(N - n)!} \quad (10.1.4)$$

When $g_1 = g_2 = 1$, this reduces to

$$\Omega_2 = \frac{N!}{n!(N - n)!} \quad (10.1.5)$$

This particular distribution prevails when at most one particle can be associated with a given set of filled states ($p = 1$), the remainder being empty.

Every possible listing of n_i values for which $\sum_i n_i = N$ leads to a different value of Ω_B in Eq. (10.1.2). The question then arises: which of the enormous number of possible Ω_B states is actually encountered in nature? Here we introduce the natural assumption of *equal a priori probabilities*, whereby every assignment of the various possible occupation values n_i is equally likely to be encountered. As is rendered plausible by the special case taken up in footnote 3, the different Ω_B values represent relative probabilities of encountering the corresponding n_i distributions. In light of the a priori assumption for the equal likelihood of all possible configurations (with minor error that we ignore), the one most likely to be found corresponds to the maximum value of $\Omega_B = \Omega_B(N, n_i)$. We will later learn how to identify that special distribution. Meanwhile we note a well established fact: for large numbers of elementary particles, the maximum value Ω_m that corresponds to the special distribution is exceedingly much larger than Ω values which correspond to any other possible distribution. Thus, the physical state corresponding to Ω_m is encountered with overwhelming probability at equilibrium. However, random temporary excursions occurring as fluctuations to neighboring states are to be expected.

Now, another question arises: what are the consequences of rendering all the marbles indistinguishable? Here we consider two points: in examining one particular shortened sequence, note that if three marbles a, b, and c are to be placed in box i , the six possible configurations $\dots(abc)_i\dots, \dots(acb)_i\dots, \dots(cab)_i\dots$, etc. are all subsumed as a unit under the same configuration; what matters is the number of marbles in the box, not their internal configuration. Thus, for all intents and purposes, these three marbles are already indistinguishable (footnote 2 supplies an illustration of this effect). Second, when the marbles are indistinguishable, there is only a single way of lining them all up initially. The factor $N!$ must then be dropped. Then, as an approximation we write

$$\Omega_{BC} = \prod_i \frac{g_i^{n_i}}{n_i!}. \quad (10.1.6)$$

This manner of introducing indistinguishability as an afterthought is clearly unsatisfactory; we will shortly introduce the proper methodology. However, the above result may be considered as a *corrected Boltzmann formula*, serving as an approximation, whose range of validity must be established by comparison with the exact results that we now take up.

Bose–Einstein Statistics

We consider the statistics relating to N fundamental particles that are indistinguishable at the outset and that are to be distributed among available energy levels without any restriction on the number that can be accommodated in any level. It is simplest to proceed with a specific representative example involving photons. Consider a collection of N harmonic oscillators, with equally spaced energy levels; a fixed energy E is to be divided in quantum units ε among these oscillators. We ask in how many distinct ways the $r = E/\varepsilon$ elementary units may be shared. This process is best visualized by examining two representative arrangements of 15 energy quanta among 9 boxes, as illustrated in Figure 10.1.1.

Note the existence of empty bins. The distribution problem of counting the number of possible configurations is now equivalent to finding the number of ways in which the 15 identical units x and the 8 identical moveable walls $|$ can be made to fit between the fixed end walls. More generally

|x| |xxx|x|xx|xx| |xxxx|xx| |xxxxx| |x| |xxxx| |xx| |xxx|

FIGURE 10.1.1

Two representative distributions of 15 objects, labeled x, among 9 boxes; empty bins are designated by |.

we ask: how many different sequences involving r quanta and $N - 1$ moveable walls can be so generated. This problem was tackled in the last section: there being no degeneracies we find that (Eq. (10.1.4))

$$\Omega_{BE} = \frac{(N + r - 1)!}{r!(N - 1)!}. \quad (10.1.7)$$

To render this applicable to the physical situation, we divide quantum space into g_k elementary cells, derived from the quantized energy levels ϵ_k and associated degeneracy g_k (the number of available states with the particular energy ϵ_k). Given a particular value of the quantization vector k , let n_k identical particles be distributed over the g_k states; for a given k , the number of distinct configurations is then found to be

$$\Omega_k = \frac{(n_k + g_k - 1)!}{n_k!(g_k - 1)!}, \quad (10.1.8a)$$

and the total number of distinct configurations is seen to be

$$\Omega_{BE} = \prod_k \frac{(n_k + g_k - 1)!}{n_k!(g_k - 1)!}, \quad (10.1.8b)$$

which is known as the *Bose–Einstein distribution law*. This simplified approach should be supplanted with a more rigorous derivation found in textbooks on quantum statistics.

Fermi–Dirac Statistics

This case relates to the physical situation where all elementary particles are indistinguishable and where any one of the g_i degenerate states of energy ϵ_i can be occupied by at most one such particle. The possible arrangements now involve the number of ways in which n_i occupied states (i.e. number of particles) can be selected from a total of $g_i > n_i$ states. We dealt with this problem in Eq. (10.1.5), which now reads

$$\Omega_{FD} = \prod_i \frac{g_i!}{n_i!(g_i - n_i)!}, \quad (10.1.9)$$

where we have taken account of all possible values for n_i and g_i .

Parenthetically, it is easy to verify that all three cases may be subsumed under the general relationship

$$\Omega_g = \prod_i \frac{g_i(g_i - r)(g_i - 2r) \dots ([g_i - (n_i - 1)]r)}{n_i!}. \quad (10.1.10)$$

Here $r = 0, 1$, or -1 for boltzons, fermions, or bosons, respectively. This is established by writing out the factorial products and then cancelling identical terms in the numerator and denominator.

10.2 The Boltzmann Relation for the Entropy

We now provide a heuristic explanation for the famous Boltzmann formula, $S = k_B \ln \Omega$, following the discussion in R.S. Berry, S.A. Rice, J. Ross.⁴ Consider two systems A and B forming an isolated compound unit I , with a constant volume V and a constant number N of particles, and maintained at constant energy $E_I = E_A + E_B$. Let $\Omega_A(E_A)$, $\Omega_B(E_B)$ represent the total number of microstates accessible by A or B, respectively. The combined number of such states is then given by

$$\Omega_I(E_I, E_A) = \Omega_A(E_A)\Omega_B(E_I - E_A) = \Omega_I(E_A), \quad (10.2.1)$$

where the quantity E_I has been dropped on the right from the list of independent variables. Consider the contribution to $\Omega_I(E_A)$ achieved with different subdivisions of the energy between the A and B components. The probability of encountering I in a particular energy state between E_A and $E_A + dE_A$ is given by $\Omega_I(E_A)/\sum_{E_A} \Omega_I(E_A) \equiv C^{-1}\Omega_A(E_A)$. C sums over all possible E_A . Using the above, the probability of finding the compound unit in the energy range E_A to $E_A + dE_A$ is given by

$$\mathcal{P}(E_A) = C^{-1}\Omega_A(E_A)\Omega_B(E_I - E_A). \quad (10.2.2)$$

Because of conservation of energy, as Ω_A rises Ω_B falls. The above product therefore has a particular value of E_A at which \mathcal{P} is at a maximum, which is extremely sharply peaked around E_A : for, Ω_A and Ω_B change very rapidly with their respective independent variables.

The maximum is located through the requirement ($P_m \equiv \mathcal{P}$)

$$\left(\frac{\partial P_m(E_A)}{\partial E_A}\right)_{V,N} = 0 = C^{-1}\Omega_B(E_I - E_A)\left(\frac{\partial \Omega_A}{\partial E_A}\right)_{V,N} + C^{-1}\Omega_A(E_A)\left(\frac{\partial \Omega_B}{\partial E_A}\right)_{V,N}. \quad (10.2.3)$$

Now divide both sides by $P(E_A)$, invoke Eq. (10.2.2), and $E_A = E_I - E_B$. Then the above relation may be cast in the form

$$\left(\frac{\partial \ln \Omega_A}{\partial E_A}\right)_{V,N} = \left(\frac{\partial \ln \Omega_B}{\partial E_B}\right)_{V,N}, \quad (10.2.4)$$

which is exactly of the form for the equilibrium condition for two phases $(\partial S_A/\partial E_A)_{V,N} = (\partial S_B/\partial E_B)_{V,N}$ derived on the basis of classical thermodynamics. It is thus apposite to postulate the *fundamental relation*

$$S = k_B \ln \Omega, \quad (10.2.5)$$

which was posited by Boltzmann from general considerations as one of the cornerstones of statistical mechanics. Thereby the thermodynamic entropy has been tied to the underlying statistics of the microvariables that characterize the state of the system. The quantity k_B , known as the *Boltzmann constant*, is inserted to satisfy the dimensionality requirements for the entropy.

10.3 Distribution Functions

To obtain a relation for the distribution of particles among energy levels ε_i in any of the above approximations, we look for the maximum value of S , i.e., of $\ln \Omega$, subject to the constraints

that $N = \sum_i n_i$ and $E = \sum_i n_i \varepsilon_i$ be fixed for the isolated system. Now $\Omega = \Omega(E, V, N)$, whence at constant V ,

$$d \ln \Omega = \left(\frac{\partial \ln \Omega}{\partial N} \right)_{V,E} dN + \left(\frac{\partial \ln \Omega}{\partial E} \right)_{V,N} dE \equiv \alpha dN + \beta dE = dS/k_B, \quad (10.3.1)$$

where the indicated definitions of α and β have been adopted. These intensive quantities are to be held fixed, so that upon integration,⁷ we obtain

$$\ln \Omega = \alpha N + \beta E, \quad (10.3.2)$$

whose maximum is specified by

$$\partial(\ln \Omega - \alpha N - \beta E)/\partial n_i = 0. \quad (10.3.3)$$

With $N = \sum_i n_i$ and $E = \sum_i n_i \varepsilon_i$, we then find that

$$\partial \ln \Omega / \partial n_i - \alpha - \beta \varepsilon_i = 0. \quad (10.3.4)$$

To determine the first term, we invoke Eq. (10.1.10) as

$$\ln \Omega = \sum_i \{ \ln g_i + \ln(g_i - r) + \dots + \ln[g_i - (n_i - 1)r] \} - \sum_i \{ \ln n_i + \ln(n_i - 1) + \dots + \ln 2 + \ln 1 \}. \quad (10.3.5)$$

Next, determine the change in $\ln \Omega$ when n_i is replaced by $n_i + 1$; on subtraction from Eq. (10.3.5), we find that

$$\Delta \ln \Omega / \Delta n_i = \ln(g_i - n_i r) - \ln(n_i + 1), \quad (10.3.6)$$

and insert this relation into Eq. (10.3.4) to obtain

$$\ln(g_i - n_i r) - \ln(n_i + 1) - \alpha - \beta \varepsilon_i = 0. \quad (10.3.7)$$

Ordinarily, we may safely neglect unity with respect to n_i to get to our final relation

$$n_i = \frac{g_i}{e^{\alpha + \beta \varepsilon_i} + r}, \quad (10.3.8)$$

which pertains to the particular equilibrium distribution for which S has its maximum value, and which is therefore the distribution prevailing at equilibrium.

Let us first consider in detail the classical approximation where $r = 0$; then

$$n_i = e^{-\alpha} g_i e^{-\beta \varepsilon_i} \quad (10.3.9a)$$

$$N = \sum_i n_i = e^{-\alpha} \sum_i g_i e^{-\beta \varepsilon_i}, \quad (10.3.9b)$$

which specifies, for any i of our choice, how many particles inhabit the state of energy ε_i . Thus, the probability of encountering that particular level in an occupation state n_i is given by

$$p_i = \frac{n_i}{N} = \frac{g_i e^{-\beta \varepsilon_i}}{q}. \quad (10.3.10a)$$

Here we have introduced

$$q \equiv \sum_i g_i e^{-\beta \varepsilon_i} \quad (10.3.10b)$$

as the standard expression for the *molecular partition function*. As will soon become obvious, this object is the workhorse for linking the microscopic properties of matter to their macroscopic properties. The manner in which it is employed is shown in Section 1.12.

It follows immediately that the ground state ($\varepsilon_i = 0$) is specified by $p_i^0 = g_i/q$, whence

$$p_i = p_i^0 e^{-\beta \varepsilon_i} \quad \text{and} \quad n_i = n_i^0 e^{-\beta \varepsilon_i} \quad (10.3.10c)$$

specifies the occupancies relative to those of the ground state.

It remains to determine the unspecified parameters α and β in Eq. (10.3.8). From

$$dS = dE/T + (P/T)dV - (\mu/T)dN = d(k_B \ln \Omega) \quad (10.3.11)$$

and the defining relation (10.3.1), as well as from Eq. (10.2.5), we find that

$$k_B \beta = \left(\frac{\partial k_B \ln \Omega}{\partial E} \right)_{V,N} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T}; \quad \beta = \frac{1}{k_B T}. \quad (10.3.12)$$

Thus, β involves the reciprocal of the thermodynamic temperature. Further,

$$k_B \alpha = \left(\frac{\partial k_B \ln \Omega}{\partial N} \right)_{V,E} = \left(\frac{\partial S}{\partial N} \right)_{V,E} = -\frac{\mu}{T}; \quad \alpha = -\frac{\mu}{k_B T} = -\beta \mu, \quad (10.3.13)$$

showing that α is related to the reduced chemical potential. The distribution function (10.3.8) may thus be recast in the final form

$$n_i = \frac{g_i}{e^{(\varepsilon_i - \mu)/k_B T} + r}. \quad (10.3.14)$$

Note that in the classical approximation, $r = 0$; then $n_i/g_i = 1/e^{\alpha + \beta \varepsilon_i}$. Since all exponents in the denominator are positive and large (especially at higher energies), it is clear that $n_i/g_i \ll 1$ serves as the criterion for the applicability of the corrected Boltzmann distribution law. Systems satisfying this criterion are said to be *dilute*, in the sense that available states vastly outweigh the number of particles for distribution.

In applying Eq. (10.3.14), one usually deals with a situation where the thermal energy $k_B T$ greatly exceeds the spacing between adjacent energy levels ε_i . One may then replace the discrete set of energies by an ε continuum. The discrete degeneracies g_i are replaced by the so-called *density of states* (DOS) *function* $g(\varepsilon)$, which provides the number of states, per unit volume of the system, within an infinitesimal range $d\varepsilon$ about the ε value of interest. This function must be specified via fundamental principles for the particular physical situation under study, and is thus considered known. For example, the DOS for free electrons in a metal in standard notation is given by

$$g(\varepsilon) = \frac{1}{2\pi^2} \left(\frac{2m_e}{\hbar^2} \right)^{3/2} \varepsilon^{1/2}, \quad (10.3.15)$$

and the spectral density of the frequency of electromagnetic radiation in standard notation is specified by

$$g(\nu) = \frac{8\pi\nu^2}{c^3}. \quad (10.3.16)$$

Thus, in the continuum scenario, Eq. (10.3.14) for the average number of particles associated with energy ε is replaced by

$$n(\varepsilon) = g(\varepsilon) \frac{1}{e^{(\varepsilon - \mu)/k_B T} + r}, \quad (10.3.17)$$

so that it is sensible to regard the second factor as specifying the *probability* $p(\varepsilon)$ of encountering the system of indistinguishable noninteracting particles in a state of energy ε relative to their chemical potential when equilibrated at temperature T . Thus,

$$p(\varepsilon) = \frac{1}{e^{(\varepsilon - \mu)/k_B T} + r}. \quad (10.3.18)$$

In dealing with photons, $r = -1$, it should be noted that $\mu = 0$, as was explained in conjunction with Eq. (5.6.14). This has to do with the fact that any number of photons may be generated if sufficient energy is available, so that the photon density is no longer an independent variable but a function of T .

10.4 Digression on the Concepts of Work and Heat

The above provides some insight into the interpretation of the concepts of work and heat at the molecular level, which up to now has eluded our grasp. Let us write out the expression for the energy of the system in terms of its various different energy levels as indexed by i : $E = \sum_i n_i \varepsilon_i$. Now consider an energy increment of the form

$$dE = \sum_i \varepsilon_i dn_i + \sum_i n_i d\varepsilon_i. \quad (10.4.1)$$

The second term may be rewritten as $\sum_i n_i (\partial \varepsilon_i / \partial \ell) d\ell$, where ℓ is the displacement; $-(\partial \varepsilon_i / \partial \ell)$ is then the force acting in the direction of decreasing energy, whence minus the second term represents the work performed on the system. This leaves the first term as representing the heat transfer. According to this interpretation, work done on a system represents a change in disposition of the energy levels of the system at fixed n_i values. The first term relates to the heat transfer, which results in a change in occupancy of the fixed energy levels of the system; with rising T , the higher lying energy levels are progressively more occupied at the expense of the lower levels, thereby beginning to even out the degree of occupancy of all levels. Of course, both processes occur in tandem, thus producing both a shift in levels on the energy scale and their occupation. This shows that one cannot separate out how much each component contributes to the energy in terms of the internal rearrangement of particles among shifting levels.

10.5 Statistical Representation of Functions of State

For a dilute system, we begin with applying the corrected Boltzmann statistics to the Boltzmann representation of the entropy:

$$S = k_B \ln \left(\prod_i \frac{g_i^{n_i}}{n_i!} \right) = k_B \sum_i (n_i \ln g_i - n_i \ln n_i + n_i) = k_B \sum_i n_i \left(\ln \frac{g_i}{n_i} + 1 \right), \quad (10.5.1)$$

where *Stirling's abbreviated approximation* to factorials of large numbers, $\ln N! \approx N \ln N - N$ has been employed as a standard operating procedure. Now introduce Eq. (10.3.9) as well as $E = \sum_i n_i \varepsilon_i$ and $N = \sum_i n_i$ to write

$$\begin{aligned} S &= k_B \sum_i n_i \left(\ln \frac{q}{N} + \beta \varepsilon_i + 1 \right) = k_B \ln \frac{q}{N} \sum_i n_i + k_B \beta \sum_i n_i \varepsilon_i + k_B \sum_i n_i \\ &= k_B N \ln(q/N) + E/T + k_B N = k_B \ln q^N - k_B (N \ln N - N) + E/T \\ &= k_B \ln(q^N / N!) + E/T, \end{aligned} \quad (10.5.2)$$

where, at the end, Stirling's approximation has been used in reverse. Note how the molecular partition function q , Eq. (10.3.10b), makes its appearance here. Note further we assumed that the constituents of the system are indistinguishable and that the system is dilute, in the sense that the classical

approximation to the Boltzmann distribution function could be employed. If the particles are distinguishable, the $N!$ factor in the last equation must be erased.

We can use another string of equalities to express the energy of the system, again in terms of the partition function, and thereby demonstrate its usefulness. This involves taking cognizance of the following differentiations:

$$-(\partial q / \partial \beta)_{V,N} = \sum_i g_i \varepsilon_i e^{-\beta \varepsilon_i}; \quad d\beta = (1/k_B)d(1/T) = -dT/k_B T^2. \quad (10.5.3)$$

Then, according to Eqs. (10.3.10a,b),

$$\begin{aligned} E &= \sum_i \varepsilon_i n_i = \frac{N}{q} \sum_i g_i \varepsilon_i e^{-\beta \varepsilon_i} = -\frac{N}{q} \left(\frac{\partial q}{\partial \beta} \right)_{V,N} = - \left(\frac{\partial \ln q^N}{\partial \beta} \right)_{V,N} \\ &= k_B T^2 \left(\frac{\partial \ln q^N}{\partial T} \right)_{V,N} = N k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_{V,N} \equiv k_B T^2 \left(\frac{\partial \ln (q^N / N!)}{\partial T} \right)_{V,N}. \end{aligned} \quad (10.5.4)$$

Note the ambiguity in the last line, which means that the relation

$$E = k_B T^2 \left(\frac{\partial \ln q^N}{\partial T} \right)_{V,N} \quad (10.5.5)$$

is applicable whether particles are distinguishable or not. In the more general case, both Eqs. (10.5.2) and (10.5.4) involve the partition function in the form $q^N/N!$; it therefore makes sense to introduce the generalized partition function as

$$Q \equiv q^N / N!, \quad (10.5.6)$$

which is known as the *canonical partition function*. Again, we must always be clear about whether the elementary units under study are distinguishable or not. If so, the $N!$ term must be erased. We then rewrite the energy as

$$E = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N}. \quad (10.5.7)$$

10.6 Summary

We conclude by a summary of final results.

TABLE 10.6.I. Summary of Results

For indistinguishable particles: $Q = q^N / N!$.

For distinguishable particles: $Q = q^N$.

Molecular partition function: $q = \sum_i g_i e^{-\varepsilon_i / k_B T}$.

Distribution function for boltzons: $n_i / N = g_i e^{-\varepsilon_i / k_B T}$.

Energy: $E = k_B T^2 (\partial \ln Q / \partial T)_{V,N}$.

Entropy: $S = k_B \ln Q + E/T$.

Helmholtz free energy: $A = E - TS = -k_B T \ln Q$.

Gibbs free energy: $G = A + PV$.

Pressure: $P = -(\partial A/\partial V)_{T,N} = k_B T (\partial \ln Q/\partial V)_{T,N}$.

Chemical potential: $\mu = (\partial A/\partial N)_{T,V} = k_B T (\partial \ln Q/\partial N)_{T,V}$.

Heat capacity at constant volume:

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{V,N} = 2k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{V,N} + k_B T^2 \left(\frac{\partial^2 \ln Q}{\partial T^2} \right)_{V,N}$$

A cautionary note: if the number of states is not much larger than the number of particles, then either Bose–Einstein or Fermi–Dirac statistics must be introduced. We do not consider the concomitant complications here.

Now, a word about the actual determination of a partition function. The actual specification of $q(g_i, \varepsilon_i)$ for important cases of interest is taken up in Section 1.12. Cases not investigated there are left to your discretion to pursue, in consultation with standard texts on statistical mechanics.

10.7 Alternative Statistical Interpretation for Entropy in Terms of Properties of a System

We now switch to a description that relates more closely to the macroscopic characteristics of a system. For this purpose, we once again consider a system A in thermal contact with a reservoir B, the two forming an isolated unit. We follow in outline the discussion by Waldram⁸ to whom the reader is referred for details that are omitted in this elementary presentation. The fundamental variable of interest is the energy E of each system, the latter being deemed sufficiently large that E may be regarded as a quasi-continuous variable; $E_A + E_B = E_T$, a constant. However, among the myriad possible combinations of energies that exist for A and B in isolation, only a limited set of states are mutually accessible, namely only those that lie in a narrow band δE of energies centered on E_T . The indeterminacy in E arises from fluctuations that are dealt within Section 1.17.

If the two components are not initially in equilibrium, heat is exchanged in a direction governed by the product $g_A g_B$ of the densities of state for the energies of A and B. This product is known to change very drastically with energy; while heat flow in the direction of decreasing $g_A g_B$ is statistically possible, the likelihood of occurrence is extremely low. In short, with overwhelming likelihood, heat flow is directed along increasing $g_A g_B$, or under conditions where

$$d \ln(g_A g_B) = d \ln g_A + d \ln g_B = (\partial \ln g_A / \partial E_A) dE_A + (\partial \ln g_B / \partial E_B) dE_B > 0, \quad (10.7.1)$$

or

$$[(\partial \ln g_A / \partial E_A) - (\partial \ln g_B / \partial E_B)] dE_A > 0. \quad (10.7.2)$$

Now if the first term in brackets exceeds the second, dE_A will necessarily increase; i.e., heat will flow into A without external intervention, which requires, according to Clausius, that A will be colder than B. Thus, $(\partial \ln g / \partial E)$ is seen to be a measure of the hotness level of a system. To quote Waldram: “A larger value of $(\partial \ln g / \partial E)$ sucks energy into itself.” Normally, g increases very rapidly with E . In light of the above, it is then sensible to postulate the association

$$1/k_B T = (\partial \ln g / \partial E), \quad (10.7.3)$$

where k_B , Boltzmann’s constant, is introduced to satisfy dimensionality requirements, and with a value so chosen as to have T coincide with the thermodynamic temperature. T so obtained is regarded as the statistical definition of temperature.

Consider now the case where B is a reservoir so huge that its temperature is rock steady at $T_B = T_R$ while fluctuations in the temperature of the system do prevail. Since the latter is anchored to the former, the temperature of the system averages around T_R , which is thus the quantity of interest. This matches the observation in Section 1.10 that in irreversible processes, it is the intensive variables of the reservoir that show up in the fundamental differential expressions for E, H, A, G . We now ask for the probability p_i that system A is encountered in a state characterized by the system energy E_i . This is proportional to the density of states of the *reservoir* g_R because it is the latter that dictates the temperature, hence energy, of the system. Using Eq. (10.7.3), we therefore write

$$(\partial \ln g_R / \partial E_R) = 1/k_B T_R = \text{const.} \quad (10.7.4)$$

from which it follows that

$$p_i \propto g_R \propto e^{E_R/k_B T_R} \propto e^{-E_i/k_B T_R}. \quad (10.7.5a)$$

The constant of proportionality is found on setting

$$\sum_i p_i = 1 \quad \text{and} \quad \sum_i e^{-E_i/k_B T_R} \equiv Z, \quad (10.7.5b)$$

where Z is now the *partition function of the system*; then

$$p_i = e^{-E_i/k_B T_R} / Z, \quad (10.7.6)$$

which is exactly the Boltzmann distribution function in terms of energies for the system. We can now construct expressions for all the items listed in the tabulation of Section 10.6, in a manner completely parallel to all the preceding derivations. Of particular interest is the entropy in the form (T is now the system temperature whose value is parameterized by the reservoir temperature T_R)

$$S = k_B \ln Z + k_B T (\partial \ln Z / \partial T)_{V,N}. \quad (10.7.7)$$

The above may be rewritten as

$$S = k_B \frac{\sum_i \exp(-E_i/k_B T)}{Z} \ln Z + k_B \sum_i \frac{E_i}{k_B T} \frac{\exp(-E_i/k_B T)}{Z} \quad (10.7.8)$$

$$S = k_B \sum_i (p_i \ln Z + p_i E_i / k_B T), \quad (10.7.9)$$

but since $\ln p_i = -E_i/k_B T - \ln Z$, and $p_i E_i / k_B T = -p_i \ln p_i - p_i \ln Z$, Eq. (10.7.9) may be recast as the fundamental relation

$$S = -k_B \sum_i p_i \ln p_i. \quad (10.7.10)$$

It is important to note that while Eq. (10.7.10) has been derived for the equilibrium state, it is generally postulated to hold as well for any other configuration of the system, and so serves as a fundamental definition for the entropy.

The following fundamental question now arises. Since, according to Eq. (10.3.10c), the occupation of the ground state is much more likely than any other why do not we encounter all macroscopic systems in or extremely close to their ground state? The answer rests on the fact that in the present

discussion we quietly passed from the statistics based on quantum states to one based on macroscopic energies. We therefore need to adjoin to the probability function p_i , based on quantum states, the density of states function g that relates to the energy distribution for macroscopic systems. This harks back to the discussion relating to Eq. (10.3.17). Thus, the energy distribution function, as opposed to the quantum states distribution function reads

$$f(E)dE = p_i(E)g(E)dE. \quad (10.7.11)$$

For virtually all systems of common interest, $g(E)$ rises faster with increasing E than $p_i(E)$ drops. As a result, f has a maximum far above the ground energy even though the occupation of the quantum states may be tiny. In fact, the maximum in $\ln f$ is given by

$$\frac{\partial \ln f}{\partial E} = -\frac{1}{k_B T} + \frac{\partial \ln g}{\partial E} = -\frac{1}{k_B T} + \frac{1}{k_B T_R} = 0, \quad (10.7.12)$$

where we invoked Eq. (10.7.4) for the reservoir. Thus, the maximum occurs at $T = T_R$, as it should.

Fluctuations in a Parameter

Let us next consider a parameter of interest that fluctuates in a small range of values dx about its equilibrium value x . This quantity characterizes in part the properties of a large system whose energy fluctuates in a range dE about its equilibrium value E . The probability that in these circumstances x lies in the indicated narrow range is given by

$$f(x) = \int g(x, E) p(E) dE, \quad (10.7.13)$$

where $p(E)$ is the distribution for classical statistics, while $g(x, E)$ is the distribution function involved in specifying the number of states wherein x and E lie, respectively, in narrow ranges dx and dE about their equilibrium values. However, if the system is sufficiently large, E may be regarded as essentially fixed and $p(E)$ essentially constant over the dE interval; then

$$f(x) \propto g(x, E), \quad (10.7.14)$$

and we may set

$$S = S(x, E) = Nk_B \ln g(x, E). \quad (10.7.15)$$

However, this simple approach fails in a number of cases that are dealt with through the cautionary tales in Waldram's treatment.⁸

FOOTNOTES

1. P.A. Rock, *Chemical Thermodynamics* (University Science Books, Mill Valley, CA, 1983).
2. Consider the word “bre₁e₂ze₃s,” in which the three e's are distinguished. We can place any of the seven letters in position 1, any of the six remaining letters in position 2, any of the five remaining letters in position 3, etc., resulting in a total of 7! scrambled “words” when the placement process is exhausted. If we now lift the distinction between the three e's, then you can easily verify that 3! of the scrambled words become indistinguishable for every sequence of the other letters, leaving 7!/3! distinguishable letter combinations based on “breezes”.
The above analogy, like many analogies, is somewhat misleading; at best, it is incomplete.
3. That Ω represents a probability may be rendered plausible by examining the simplest case of a binomial distribution, $p^n(1-p)^{N-n}N!/n!(N-n)!$, Eq. (10.1.4). When we next sum this

expression from $n = 0$ to $n = N$, we obtain the expression

$$(1 - p)^N + Np(1 - p)^{N-1} + \dots + [N(N - 1)/2]p^2(1 - p)^{N-2} + \dots + Np^{N-1}(1 - p) + p^N.$$

This sum represents the expansion of the binomial $[p + (1 - p)]^N = 1$. Thus, in this case, Ω actually is the probability of encountering a specific configuration among the myriad possible configurations enumerated in Eq. (10.1.4). When maximized, it represents the most likely, i.e., the equilibrium, configuration under the specified constraints. In more general cases one must divide the specific Ω of interest by the totality of all possible Ω s to obtain the various probabilities.

4. R.S. Berry, S.A. Rice, J. Ross, *Physical Chemistry* (Oxford University Press, 2000), 2nd Ed. p. 435–436.
5. Carry out the above process for the case $g_i = 3$, and convince yourself that the Bose–Einstein formulation is correct even when the number of particles exceeds $g_i = 3$.
6. Convince yourself that the last factor, $(g_i - n_i + 1)$ in Eq. (10.1.10) correctly accounts for the Fermi–Dirac relation when all n_i particles are distributed among g_i states associated with energy ϵ_i .
7. Show that the arbitrary constant of integration in Eq. (10.3.2) vanishes. Incidentally, α and β as used here are standard notation and are not to be confused with the thermal parameters introduced in the first three chapters.
8. J.R. Waldram, *The Theory of Thermodynamics* (Cambridge University Press, Cambridge, 1985, Chap. 3).

10.8 Derivation of Curie's Law and Ohm's Law

Curie's Law of Magnetic Susceptibility

Consider a lattice of N noninteracting spins per unit volume, each of which has a magnetic moment μ_s that interacts with an imposed magnetic field \mathcal{H} . The magnetic energy in the applied field is specified by $E_m = -\mu_s \cdot \mathcal{H} = -\mu_s \mathcal{H} \cos \theta$, where θ is the angle between the magnetic moment and the field. The total magnetization of the lattice is then given by $\mathcal{M} = N\mu_s \langle \cos \theta \rangle$, where the angular brackets denote an average over the thermal equilibrium distribution, given (in standard notation) by

$$\langle \cos \theta \rangle = \frac{\int e^{-\beta E_m} \cos \theta d\Omega}{\int e^{-\beta E_m} d\Omega} = \frac{\int_0^\pi 2\pi \sin \theta \cos \theta e^{\beta \mu_s \mathcal{H} \cos \theta} d\theta}{\int_0^\pi 2\pi \cos \theta e^{\beta \mu_s \mathcal{H} \cos \theta} d\theta}. \quad (10.8.1)$$

To simplify the derivation, introduce a new integration variable $s = \cos \theta$ and set $x = \mu_s \mathcal{H} / k_B T$, so that

$$\begin{aligned} \langle \cos \theta \rangle &= \frac{\int_{-1}^1 s e^{sx} ds}{\int_{-1}^1 e^{sx} ds} = \frac{d}{dx} \left[\ln \int_{-1}^1 e^{sx} ds \right] = \frac{d}{dx} \ln \left[\frac{e^x - e^{-x}}{x} \right] = \frac{d}{dx} \ln \left[e^x - e^{-x} \right] - \frac{d}{dx} \ln x \\ &= \text{ctnh } x - 1/x \equiv \Lambda(x), \end{aligned} \quad (10.8.2)$$

where $\Lambda(x)$ is known as the *Langevin Function*. A plot of this function is shown in Figure 10.8.1. At first, Λ rises linearly with x , but it then bends over and at $x = 5$ reaches 80% of the saturation value of unity. Thus, at sufficiently high magnetic fields, most of the magnetic moments align precisely in the

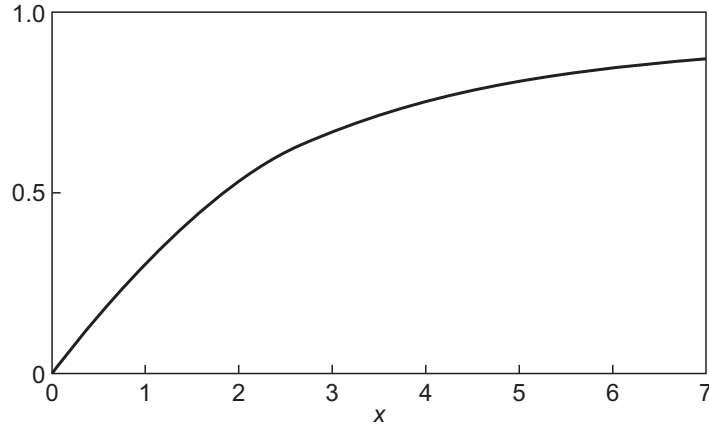


FIGURE 10.8.1

The Langevin function $\coth x - 1/x$ vs x .

direction of the field. However, normally, the magnetic energy is very small compared to room temperature, so that the zero-order expansion $\Lambda(x) = x/3$ suffices. Then,

$$\mathcal{M} = N\mu_s^2 \mathcal{H}/3k_B T; \quad \chi = N\mu_s^2/3k_B T, \quad (10.8.3)$$

which is *Curie's law*.

Specification of Ohm's Law

We consider here the free-electron model that serves as a rock bottom approximation for modeling the electronic conduction in metals. According to quantum mechanics, the momentum of a free particle is specified by $\mathbf{p} = \hbar \mathbf{k}$, where \mathbf{k} is the wave vector associated with the free-particle wave function $\psi(\mathbf{r}) = (1/V)^{1/2} e^{i\mathbf{k} \cdot \mathbf{r}}$. The force acting on an electron in an electric field \mathbf{E} is $-e\mathbf{E}$, and by Newton's Law,

$$-e\mathbf{E} = d\mathbf{p}/dt = \hbar d\mathbf{k}/dt. \quad (10.8.4)$$

In the absence of any scattering, all electron momenta are displaced by $\delta \mathbf{k} = -e\mathbf{E} \delta t$ in time δt . However, the acceleration is counteracted by the collision of electrons with impurities, displaced atoms, or atomic vibrations, so that a steady state sets in after a time lapse τ , by which the momentum increase is limited to $\hbar \delta \mathbf{k} = -e\mathbf{E} \tau$, whence the average velocity attained in the field is specified by

$$\delta \mathbf{v} = -e\mathbf{E} \tau / m. \quad (10.8.5)$$

For n electrons per unit volume of charge $-e$ each, the current density then is given by

$$\mathbf{J} = -en\delta \mathbf{v} = ne^2 \mathbf{E} \tau / m = \sigma \mathbf{E}, \quad (10.8.6)$$

which is *Ohm's law*, with the electrical conductivity σ specified as shown above. The mean free path may then be defined by $\ell = v_F \tau$, where v_F is the velocity of electrons at the Fermi surface; it is only those electrons that can respond to the electric field.

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About the Author

Prof. Jurgen M. Honig received a BS degree from Amherst College in 1945 and a PhD degree from the University of Minnesota in 1952. After a postdoctoral appointment year at the James Forrestal Center of Princeton University in 1953, he joined the Department of Chemistry at Purdue University in 1953, and was promoted to Associate Professor in 1958. From 1959 to 1967, he was Associate Group leader and Group leader at the MIT Lincoln Laboratory in Lexington, MA. He returned as Professor of Chemistry to Purdue University in 1967 and retired from that position in 2000. During the latter years, he was Editor of the Journal of Solid State Chemistry (1982–2000), the Chairman of the Materials Sciences Council (1968–1982), and published over 420 refereed publications and five books. He has earned an honorary degree from the University of Science and Technology (2009), Krakow, Poland; fellow of the New York Academy of Sciences; Wetherill medal (1995); Editor, Journal of Solid State Chemistry (1982–2000); Honorary Member, Materials Research Society of India; two issues of the Journal of Solid State Chemistry (1990 and 2000) and an issue of Solid State Sciences (2000) dedicated to him; and a session at a Materials Research Society meeting (2000) held in honor of his retirement.



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